Supporting Information for

A Ru(I) Metalloradical that Catalyzes Nitrene Coupling to Azoarenes from Arylazides

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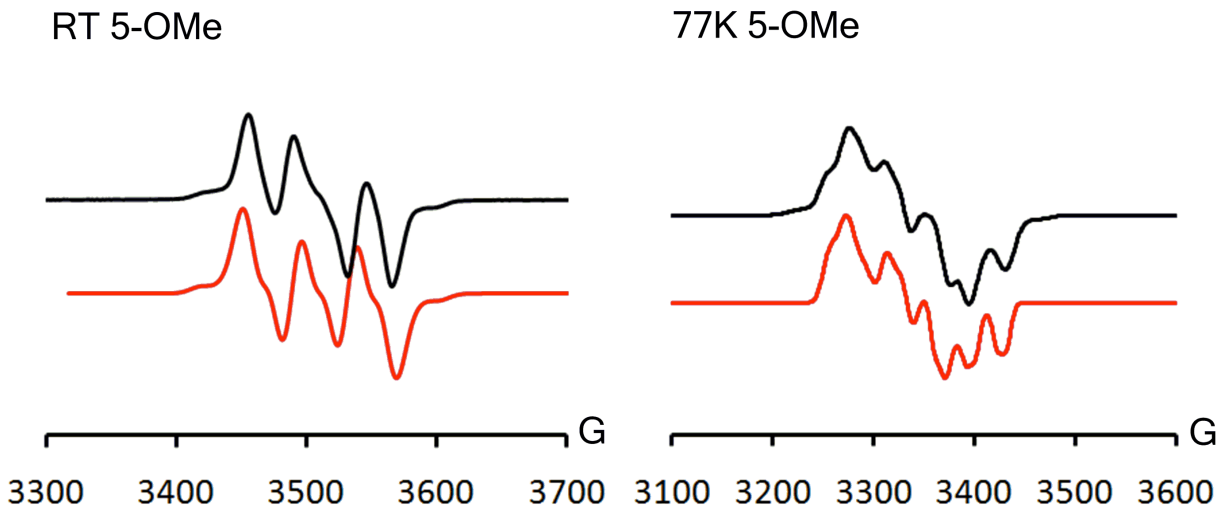
Figure 1. Room temperature (left) and 77 K (right) EPR spectrum of 5-OMe.



RT:

Experimental parameters; Microwave power, 1.011 mW; microwave frequency, 9.847 GHz; modulation amplitude, 10 G; gain, 1000; time constant, 2.560 ms.

Simulation parameters: g = 2.002. For 1 N atom, A(^{14}N) = 119 MHz. For 1 P atom, A(^{31}P) = 48 MHz. For 1 Ru atom, A(^{99}Ru) = A(^{101}Ru) = 38 MHz.

77 K:

Experimental parameters; Microwave power, 0.172 mW; microwave frequency, 9.373 GHz; modulation amplitude, 10 G; gain, 1000; time constant, 2.560.

Simulation parameters: g_x = 2.035, g_y = 2.014, g_z = 1.972; For one P atom, $A_x(^{31}P)$ = 40 MHz, $A_y(^{31}P)$ = 40 MHz, $A_z(^{31}P)$ = 20 MHz ; For one N atom, $A(^{14}N)_x$ = 80 MHz, $A(^{14}N)_y$ = 105 MHz, $A(^{14}N)_z$ = 90 MHz; lw =1, HStrain, W_x = 35 MHz, W_y = 35 MHz, W_z = 10 MHz.

Figure 2. RT EPR spectra of crude mixture (left) of stoichiometric reaction between 4 and $MeOC_6H_4N_3$ and after subtraction of 4 (right).

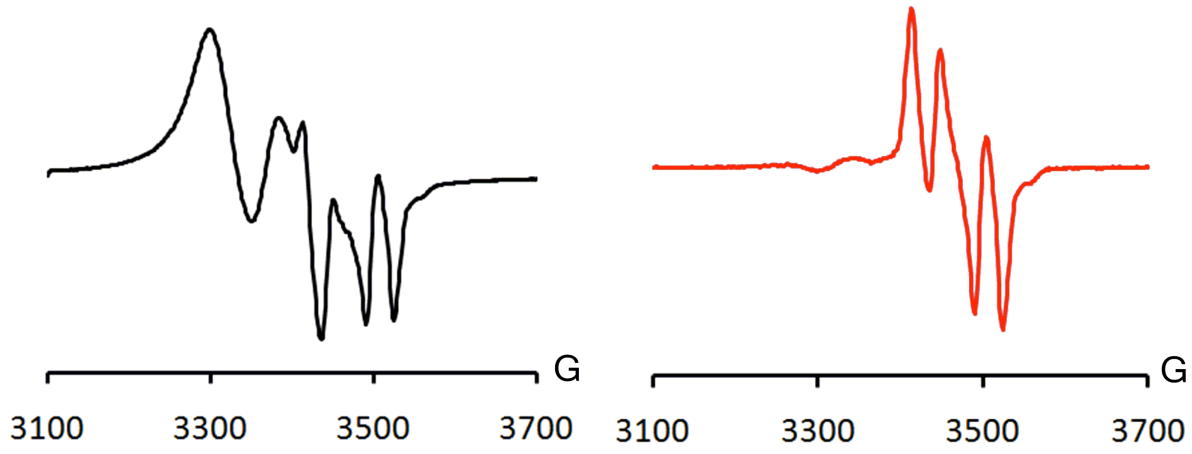


Figure 3. RT EPR spectra of crude mixture (left) of stoichiometric reaction between 4 and $EtOC_6H_4N_3$ and after subtraction of 4 (right).

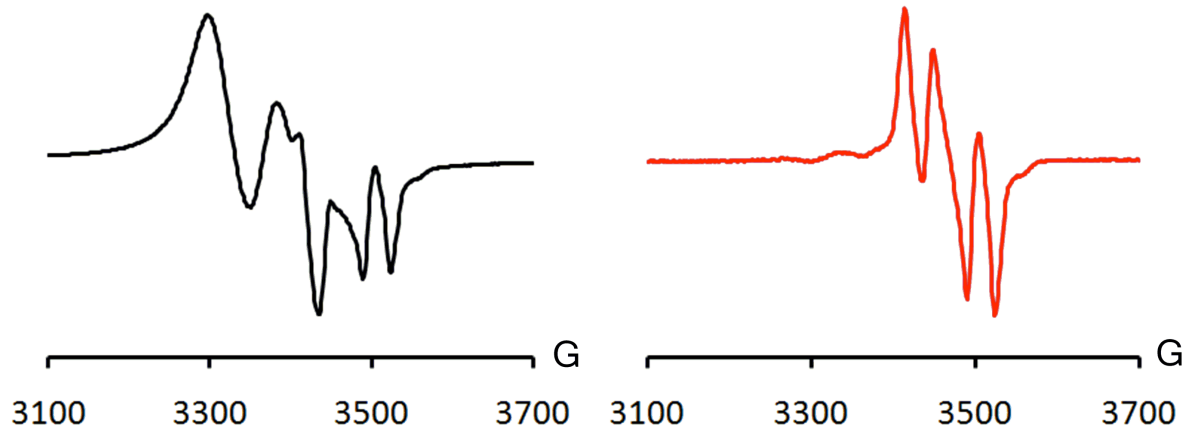


Figure 4. RT EPR spectra of crude mixture (left) of stoichiometric reaction between 4 and $MeC_6H_4N_3$ and after subtraction of 4 (right).

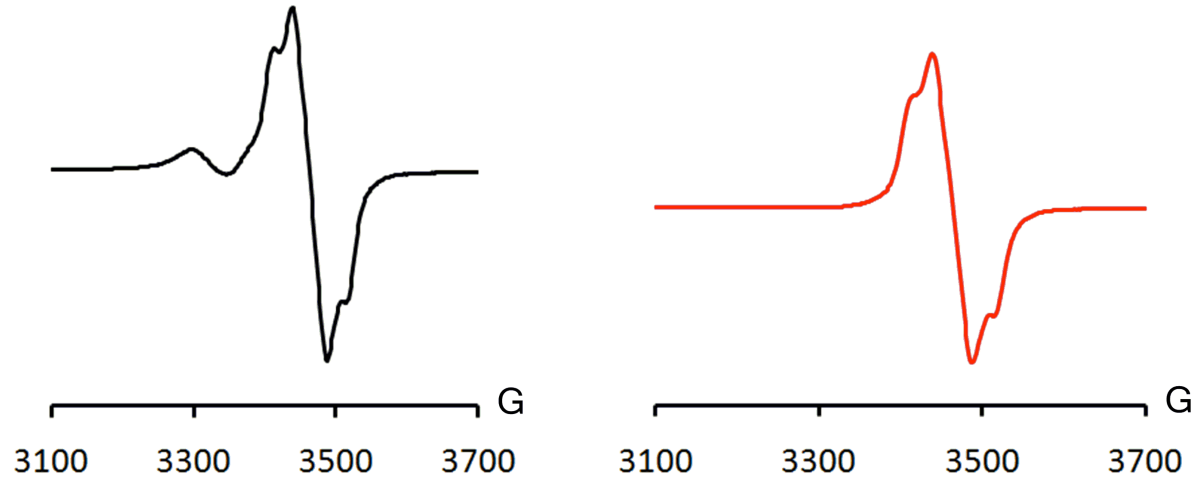


Figure 5. RT EPR spectra of crude mixture (left) of stoichiometric reaction between 4 and $MesN_3$ and after subtraction of 4 (right).

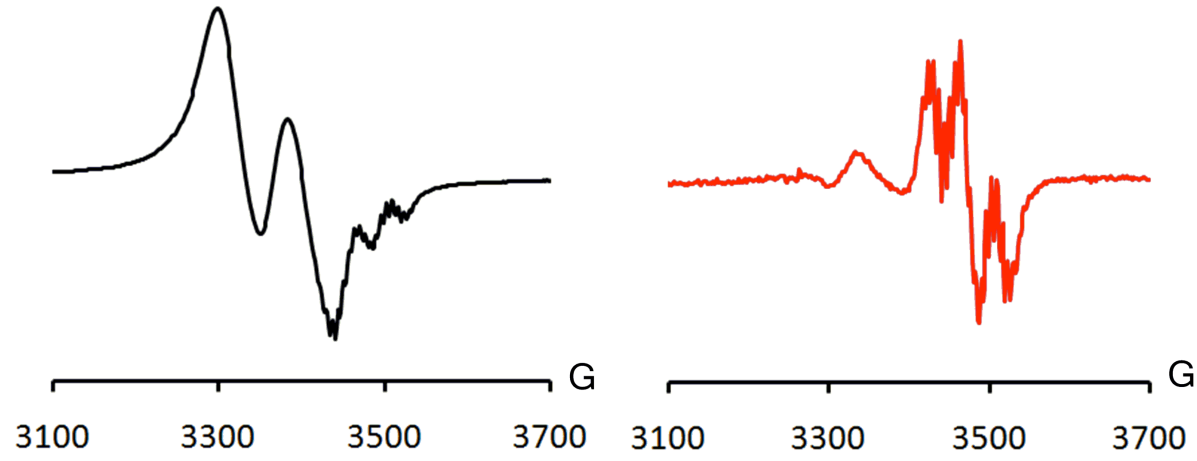
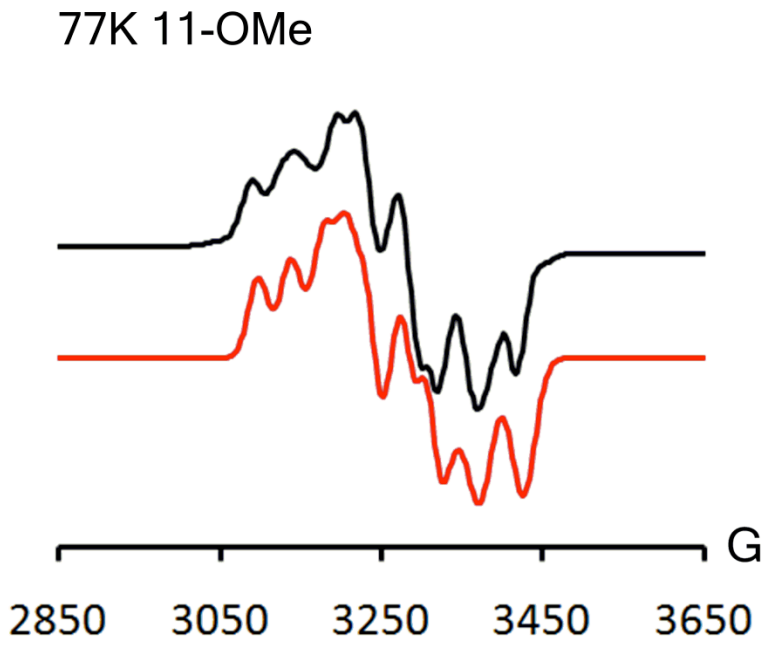


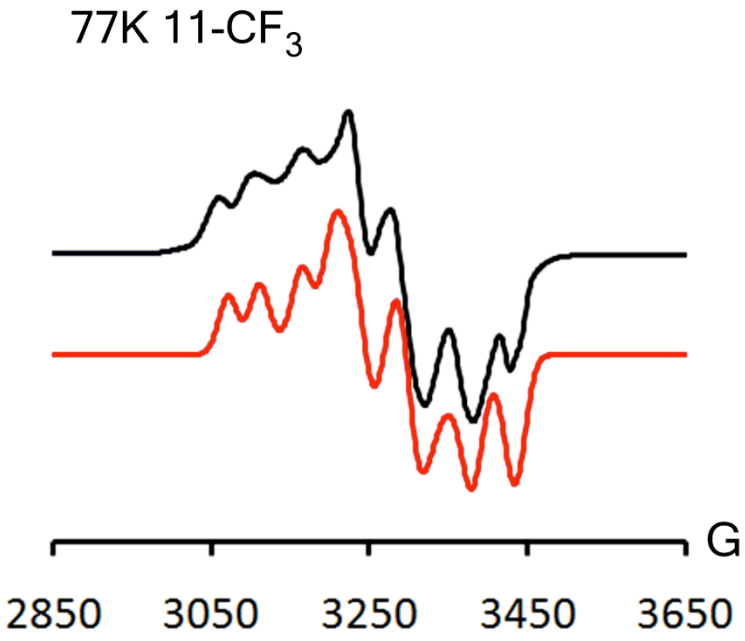
Figure 6. 77 K EPR spectrum of 11-OMe.



Experimental parameters; Microwave power, 6.454 mW; microwave frequency, 9.421 GHz; modulation amplitude, 2 G; gain, 5020; time constant, 40.960.

Simulation parameters: g_x = 2.137, g_y = 2.068, g_z = 1.985; For one P atom, $A_x(^{31}P)$ = 240 MHz, $A_y(^{31}P)$ = 210 MHz, $A_z(^{31}P)$ = 150 MHz ; For one P atom, $A(^{31}P)_x$ = 120 MHz, $A(^{31}P)_y$ = 85 MHz, $A(^{31}P)_z$ = 1 MHz; lw =1, HStrain, W_x = 80 MHz, W_y = 70 MHz, W_z = 90 MHz.

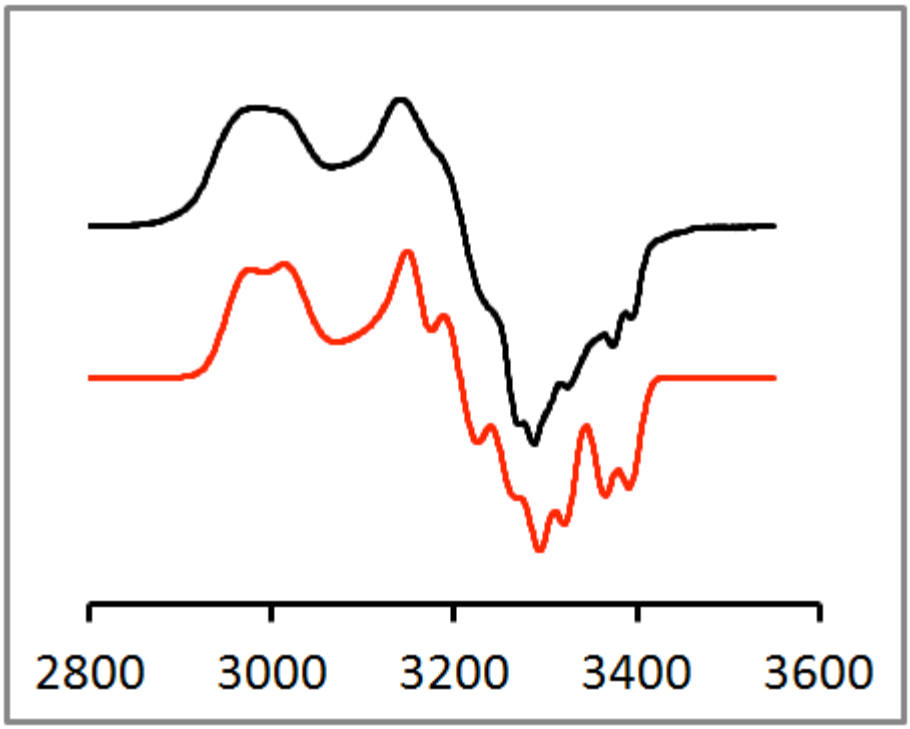
Figure 7. 77 K EPR spectrum of 11-CF_3.



Experimental parameters; Microwave power, 6.423 mW; microwave frequency, 9.442 GHz; modulation amplitude, 2 G; gain, 5020; time constant, 40.960.

Simulation parameters: g_x = 2.15, g_y = 2.063, g_z = 1.988; For one P atom, $A_x(^{31}P)$ = 280 MHz, $A_y(^{31}P)$ = 170 MHz, $A_z(^{31}P)$ = 150 MHz ; For one P atom, $A(^{31}P)_x$ = 120 MHz, $A(^{31}P)_y$ = 1 MHz, $A(^{31}P)_z$ = 1 MHz; For one P atom; lw =1, HStrain, W_x = 80 MHz, W_y =95 MHz, W_z = 80 MHz.

Figure 8. 77 K EPR spectrum of 12.



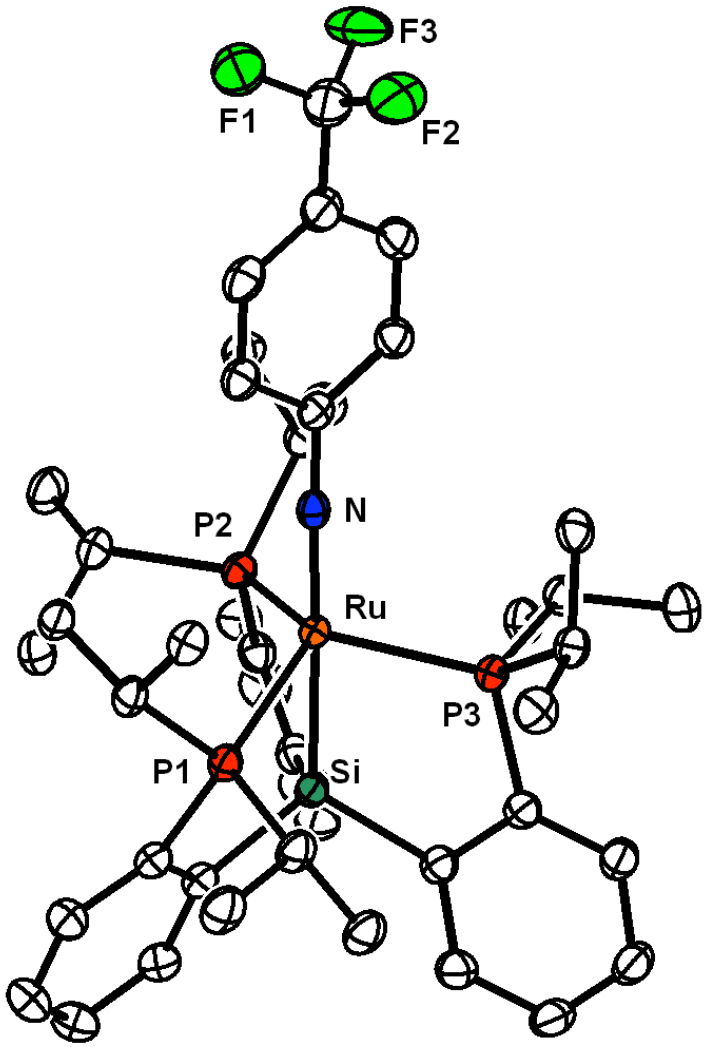
Experimental parameters; Microwave power, 0.478 mW; microwave frequency, 9.371 GHz; modulation amplitude, 10 G; gain, 1590; time constant, 2.560.

Simulation parameters: g_x = 2.275, g_y = 2.121, g_z = 2.033; For one P atom, $A_x(^{31}P)$ = 150 MHz, $A_y(^{31}P)$ = 160 MHz, $A_z(^{31}P)$ = 200 MHz ; For one P atom, $A(^{31}P)_x$ = 1 MHz, $A(^{31}P)_y$ = 100 MHz, $A(^{31}P)_z$ = 80 MHz; lw =1, HStrain, W_x = 150 MHz, W_y =55 MHz, W_z = 75 MHz.

Table 1. Crystal data and structure refinement for **{[SiP$^{i\mathrm{Pr}}_3$]Ru(NAr)}OTf (Ar = $C_6H_4CF_3$, 7-CF_3)**.

Identification code	d8-09018	
Empirical formula	C52 H66 F6 N O5 P3 Ru S Si	
Formula weight	1153.19	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 17.4556(4) Å	a= 90°.
	b = 15.9409(4) Å	b= 110.714(2)°.
	c = 20.2398(5) Å	g = 90°.
Volume	5267.8(2) Å^3	
Z	4	
Density (calculated)	1.454 Mg/m^3	
Absorption coefficient	4.440 mm^{-1}	
F(000)	2392	
Crystal size	0.48 x 0.25 x 0.02 mm^3	
Theta range for data collection	2.88 to 68.11°.	
Index ranges	-20<=h<=20, -18<=k<=18, -23<=l<=23	
Reflections collected	93228	
Independent reflections	9433 [R(int) = 0.0427]	
Completeness to theta = 33.13°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9164 and 0.2244	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8744 / 377 / 751	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0974	
R indices (all data)	R1 = 0.0355, wR2 = 0.0995	
Largest diff. peak and hole	0.898 and -0.767 e.Å^{-3}	

Figure 9. Solid-state structure of {[SiP$^{iPr}_3$]Ru(NAr)}OTf (Ar = $C_6H_4CF_3$, 7-CF_3).

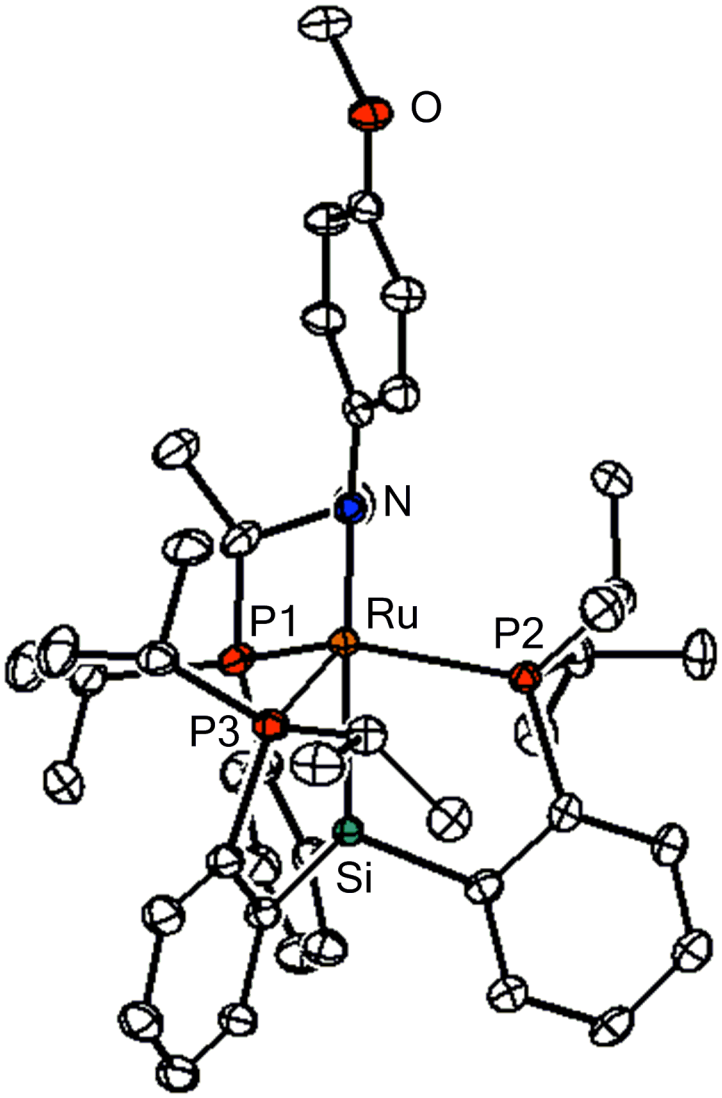


Anion, H-atoms, and solvent molecules removed for clarity.

Table 2. Crystal data and structure refinement for **{[SiP$^{i\mathrm{Pr}}_3$]Ru(NAr)}BAr$^{\mathrm{F}}_4$ (Ar = C_6H_4OMe, 7-OMe)**.

Identification code	09117	
Empirical formula	C75 H66 B F24 N O P3 Ru S Si	
Formula weight	1686.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.0069(10) Å	a= 104.3690(10)°.
	b = 15.6351(11) Å	b= 104.2060(10)°.
	c = 20.2288(15) Å	g = 99.7600°.
Volume	3745.2(5) Å^3	
Z	2	
Density (calculated)	1.495 Mg/m^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	1710	
Crystal size	0.35 x 0.25 x 0.20 mm^3	
Theta range for data collection	2.25 to 29.64°.	
Index ranges	-17<=h<=17, -20<=k<=20, -26<=l<=26	
Reflections collected	89456	
Independent reflections	9920 [R(int) = 0.0490]	
Completeness to theta = 33.13°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9254 and 0.8744	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18518 / 0 / 976	
Goodness-of-fit on F^2	1.201	
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1511	
R indices (all data)	R1 = 0.0634, wR2 = 0.1654	
Largest diff. peak and hole	1.866and -1.097e.Å^{-3}	

Figure 10. Solid-state structure of {[SiP$^{i\text{Pr}}_3$]Ru(NAr)}OTf (Ar = C_6H_4OMe, 7-OMe).

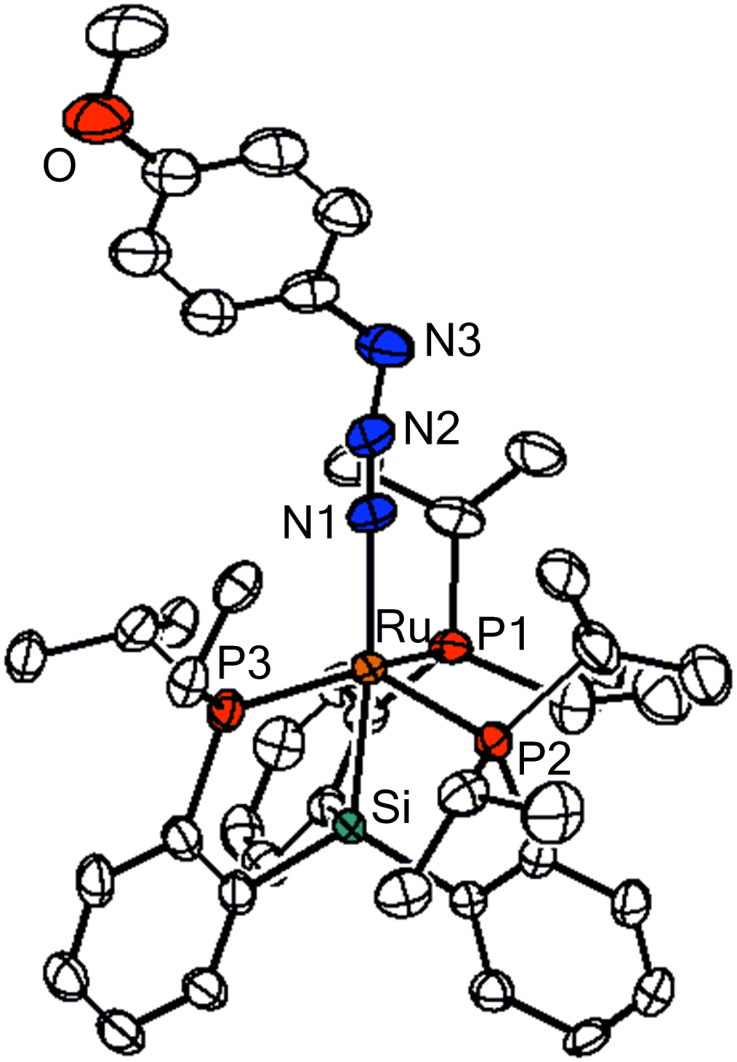


Anion, H-atoms, and solvent molecules removed for clarity.

Table 3. Crystal data and structure refinement for **{[SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar)}BAr$^{\mathrm{F}}_4$ (Ar = C$_6$H$_4$OMe, 8-OMe)**.

Identification code	09278	
Empirical formula	C75 H73 B F24 N3 O P3 Ru Si	
Formula weight	1721.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 15.1068(14) Å	a= 90.00°.
	b = 15.2076(12) Å	b= 110.504(3)°.
	c = 17.5911(16) Å	g = 90.00°.
Volume	3785.3(6) Å^3	
Z	2	
Density (calculated)	1.510 Mg/m^3	
Absorption coefficient	0.392 mm^{-1}	
F(000)	1752	
Crystal size	0.20 x 0.15 x 0.12 mm^3	
Theta range for data collection	2.20 to 30.07°.	
Index ranges	-21<=h<=20, -21<=k<=21, -24<=l<=24	
Reflections collected	87565	
Independent reflections	9846 [R(int) = 0.0796]	
Completeness to theta = 33.13°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9545 and 0.9257	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22047 / 1628 / 1055	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1309	
R indices (all data)	R1 = 0.0964, wR2 = 0.1515	
Largest diff. peak and hole	1.062 and -0.477 e.Å^{-3}	

Figure 11. Solid-state structure of {[SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar)}BAr$^{\mathrm{F}}_4$ (Ar = C$_6$H$_4$OMe, 8-OMe).

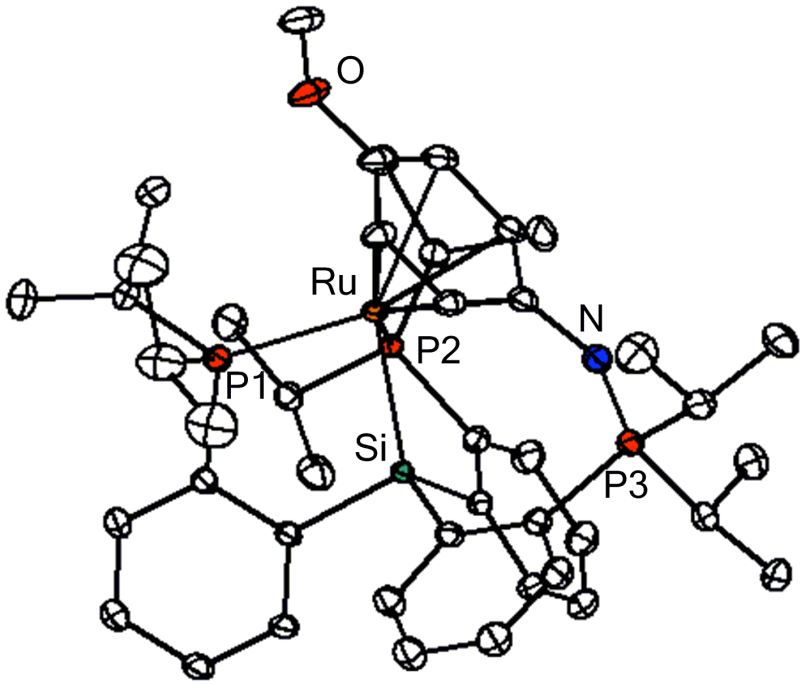


Anion, H-atoms, and solvent molecules removed for clarity.

Table 4. Crystal data and structure refinement for **{[SiP$^{iPr}_2$P^{iPr}(=NAr)]Ru}PF$_6$ (Ar = C$_6$H$_4$OMe, 10)**.

Identification code	ayt14	
Empirical formula	C47 H69 F6 N O2 P4 Ru Si	
Formula weight	1047.07	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.6608(6) Å	a= 90.00°.
	b = 13.3290(6) Å	b= 92.074(2)°.
	c = 28.9276(13) Å	g = 90.00°.
Volume	4878.5(4) Å^3	
Z	4	
Density (calculated)	1.426 Mg/m^3	
Absorption coefficient	0.538 mm^{-1}	
F(000)	2184	
Crystal size	0.38 x 0.30 x 0.29 mm^3	
Theta range for data collection	2.35 to 44.31°.	
Index ranges	-25<=h<=25, -26<=k<=26, -56<=l<=57	
Reflections collected	350218	
Independent reflections	9918 [R(int) = 0.0428]	
Completeness to theta = 33.13°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8595 and 0.8215	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	40397 / 474 / 636	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.1005	
R indices (all data)	R1 = 0.0560, wR2 = 0.1133	
Largest diff. peak and hole	2.275 and -1.046 e.Å^{-3}	

Figure 12. Solid-state structure of {[SiP$^{i\text{Pr}}_2$P$^{i\text{Pr}}$(=NAr)]Ru}PF$_6$ (Ar = C$_6$H$_4$OMe, 10).



Anion, H-atoms, solvent molecules removed for clarity.

Figure 13. Cyclic Voltammogram of 7-CF_3.

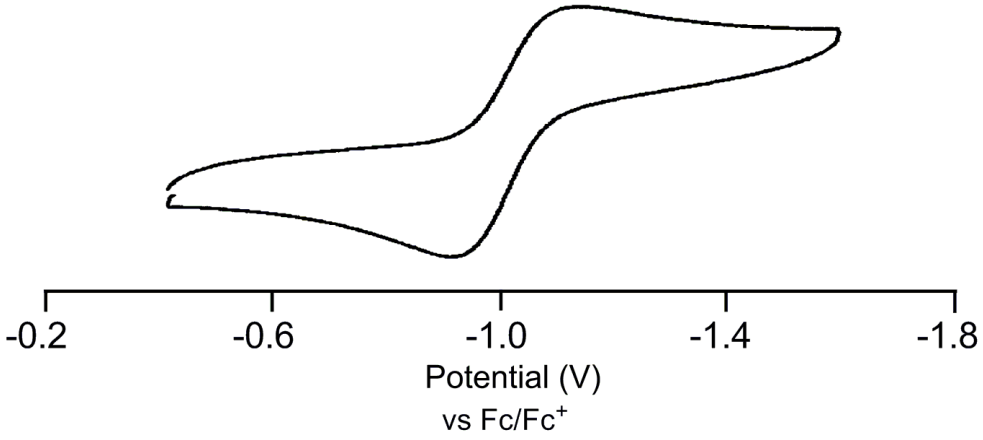
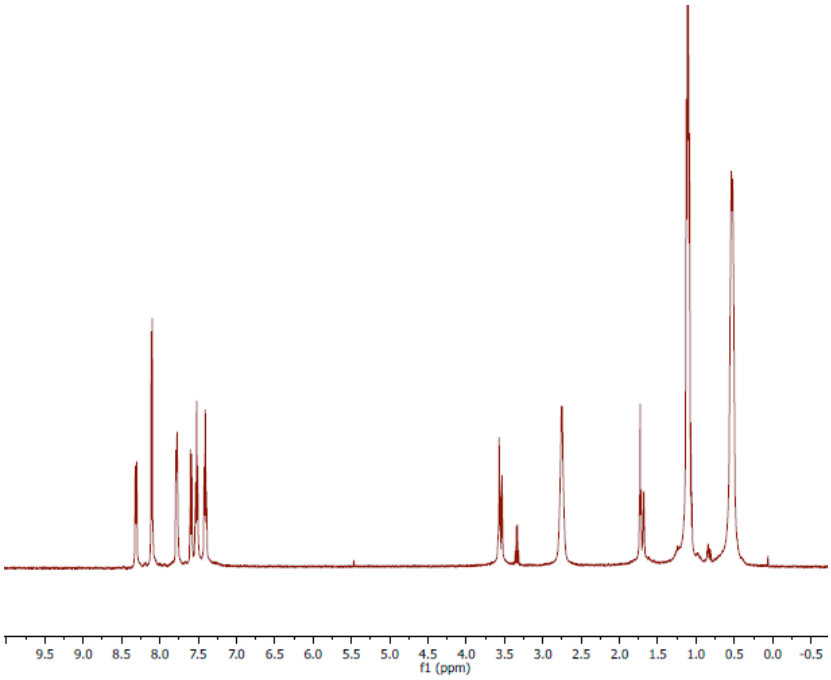
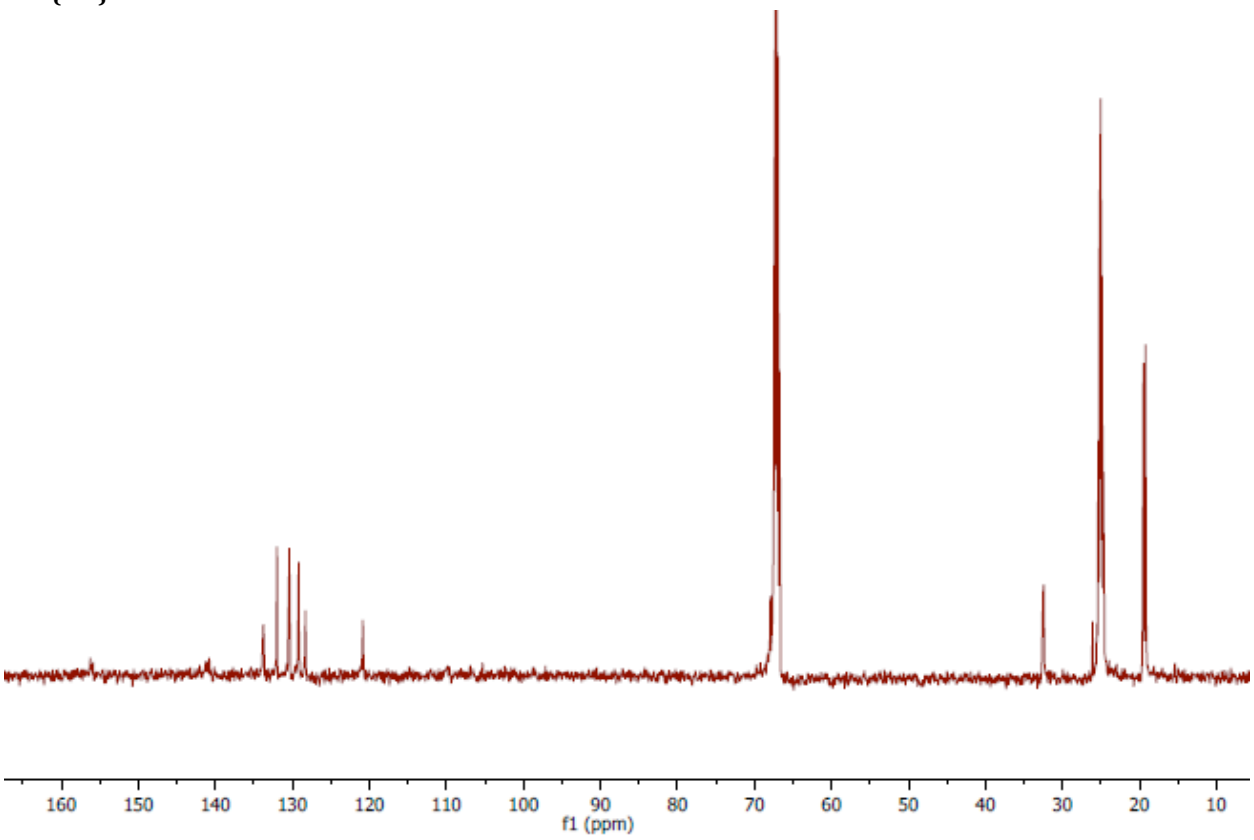


Figure 14. NMR spectra of {[SiP$^{i\mathrm{Pr}}_3$]Ru(NAr)}OTf (Ar = $C_6H_4CF_3$) (7-CF_3).

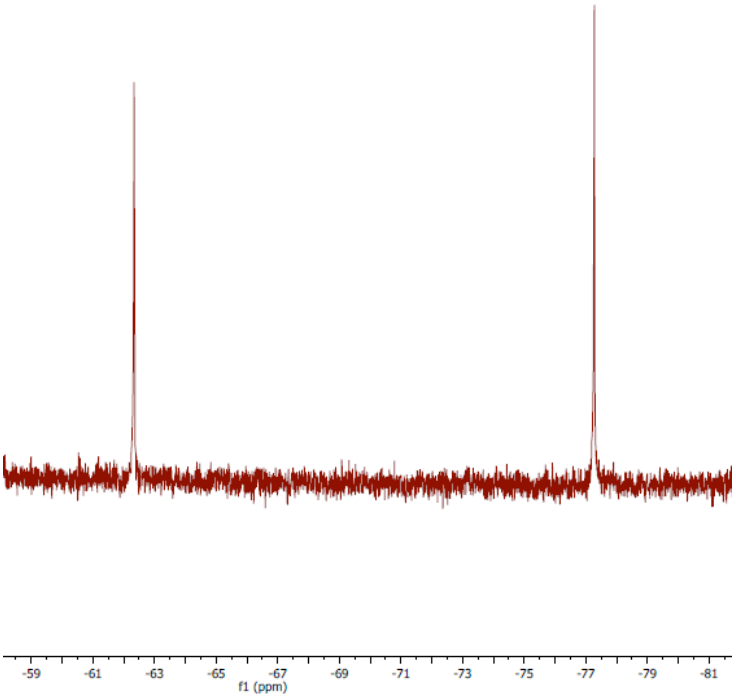
^{1}H



^{13}C{^{1}H}



$^{19}F\{^{1}H\}$


-59
-61
-63
-65
-67
-69
-71
-73
-75
-77
-79
-81
f1 (ppm)

$^{31}P\{^{1}H\}$

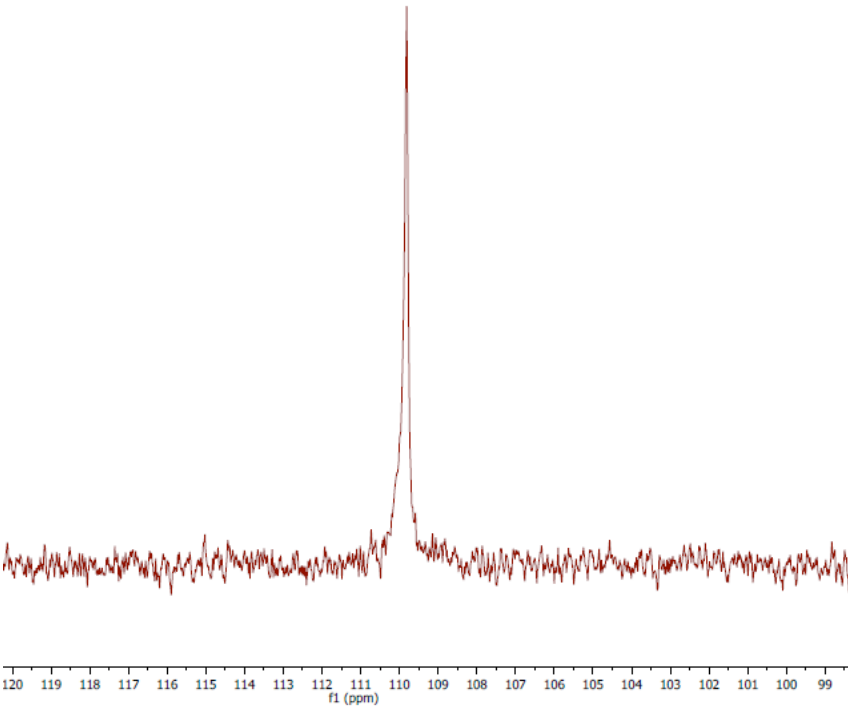
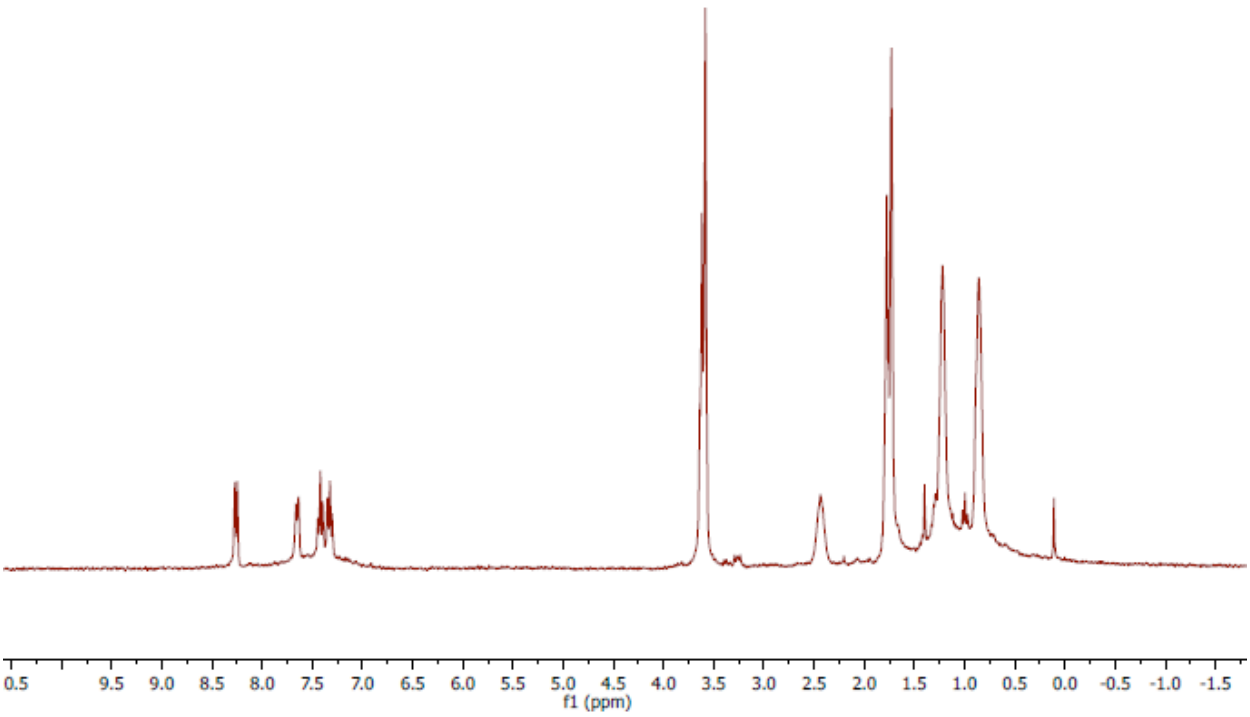
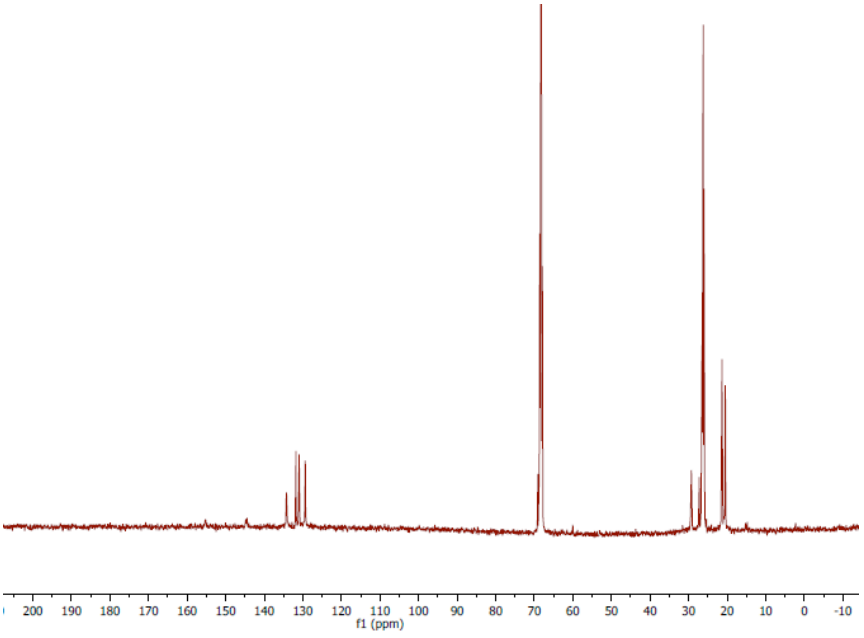
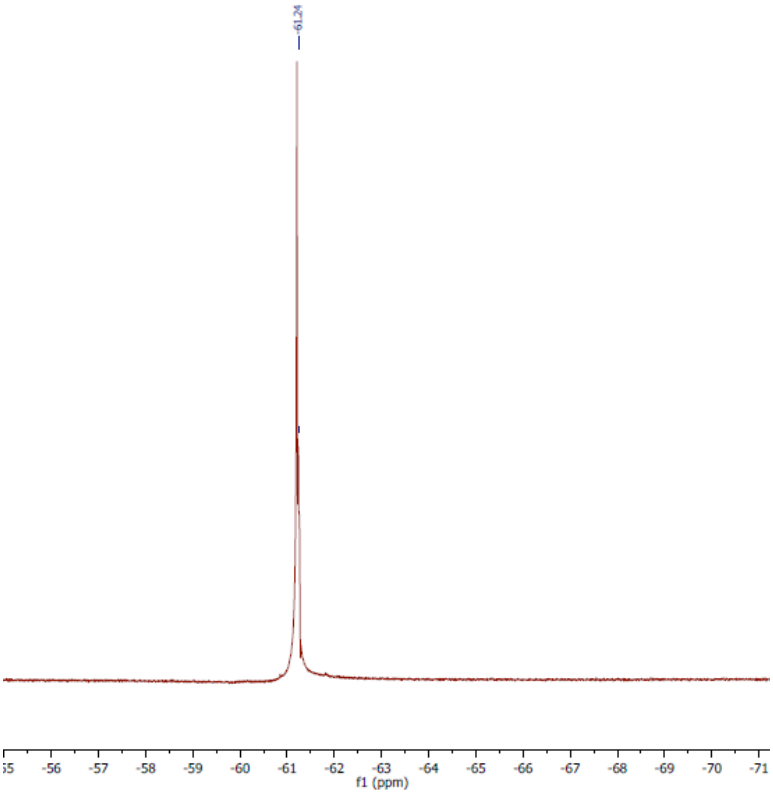

120
119
118
117
116
115
114
113
112
111
110
109
108
107
106
105
104
103
102
101
100
99
f1 (ppm)

Figure 15. NMR spectra of {[SiP$^{i\mathrm{Pr}}_3$]Ru(N_2)}PF_6 (9-PF_6).
^{1}H





$^{19}F\{^{1}H\}$


-61.24
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
f1 (ppm)

$^{31}P\{^{1}H\}$

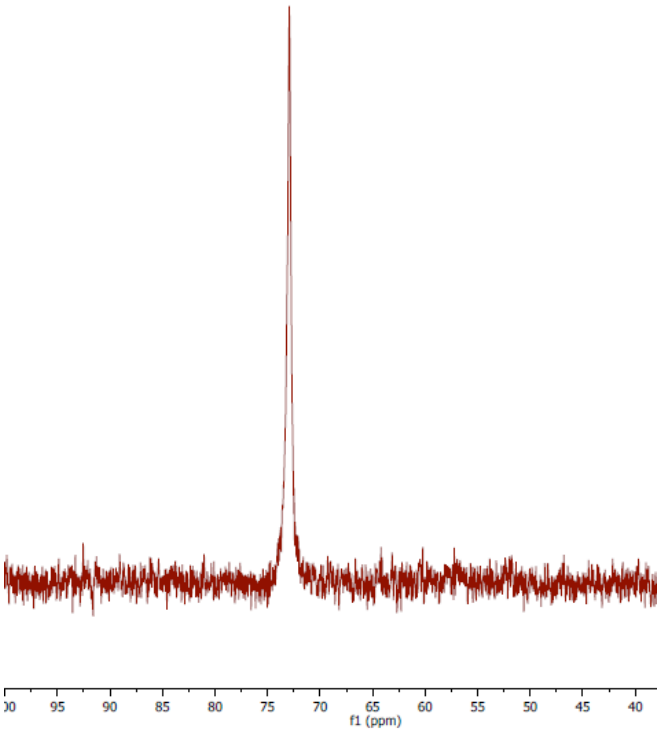
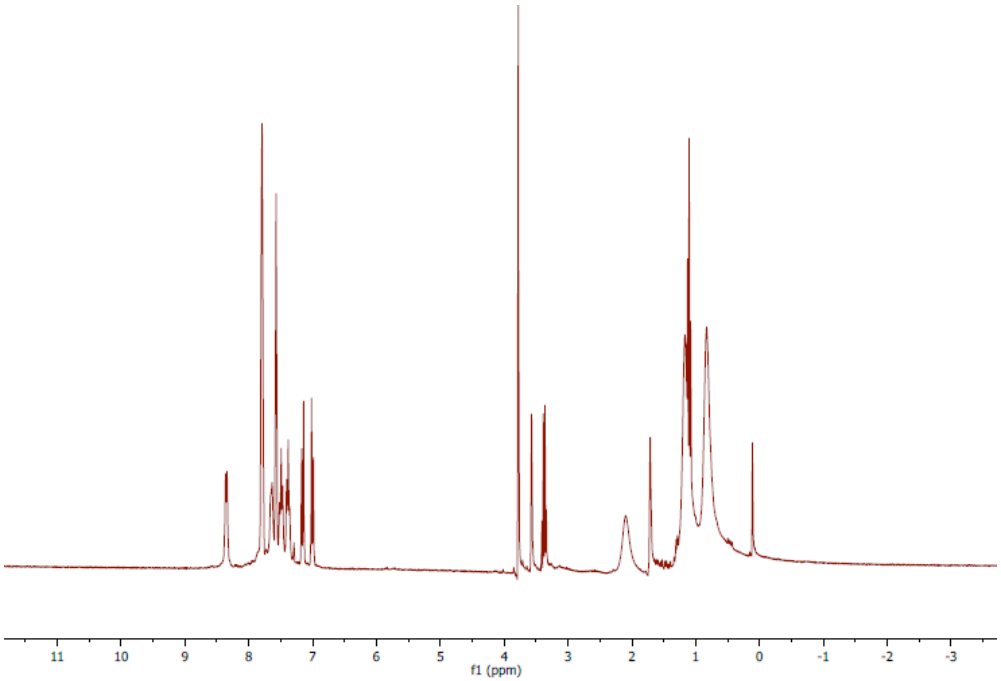
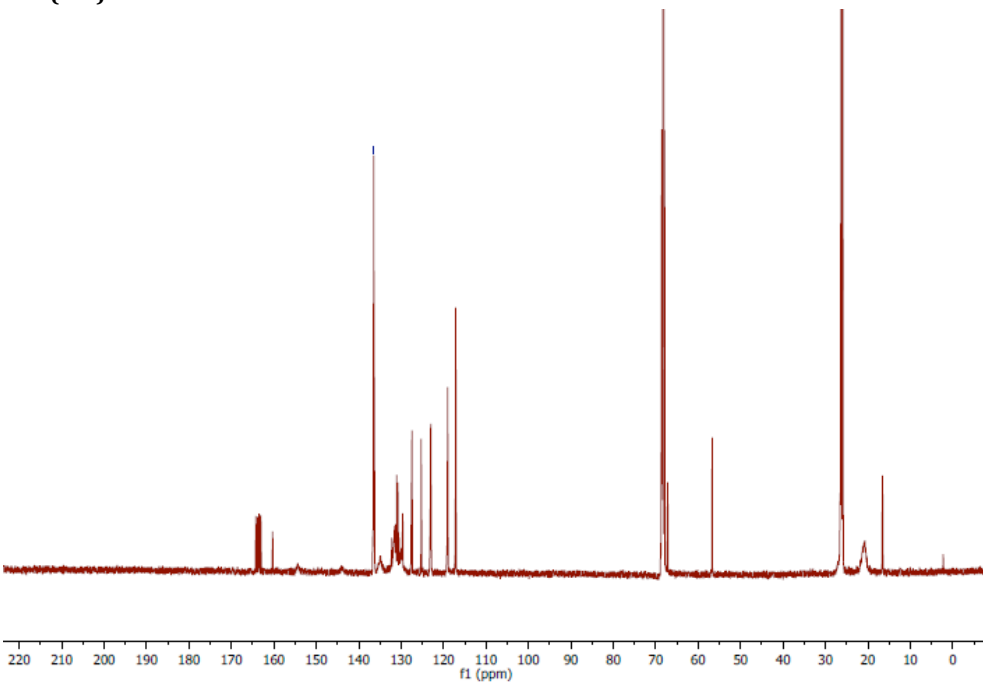

95
90
85
80
75
70
65
60
55
50
45
40
f1 (ppm)

Figure 16. NMR spectra of {[SiP$^{i\mathrm{Pr}}_3$]Ru($N_3C_6H_4$OMe)}BAr^F_4 (8-OMe).

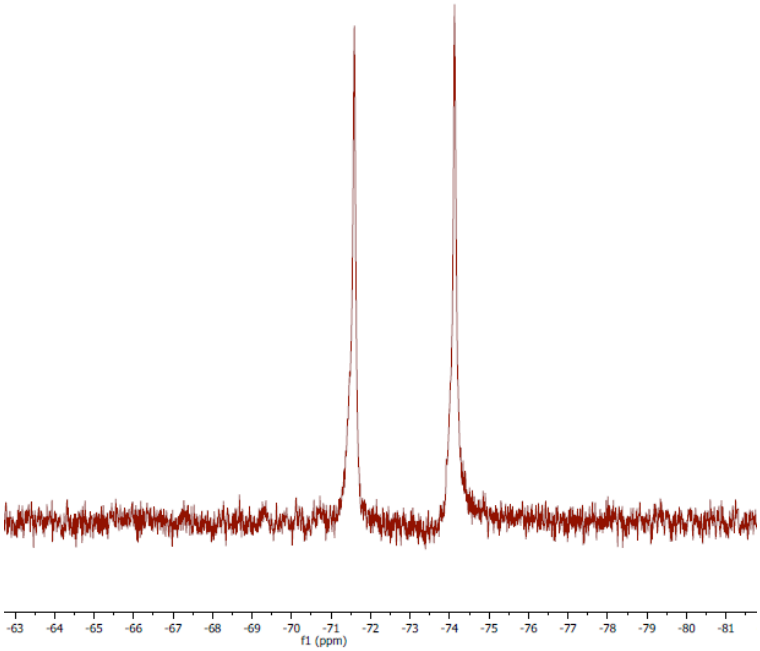
^{1}H



^{13}C{^{1}H}



$^{19}F\{^{1}H\}$


-63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81
f1 (ppm)

$^{31}P\{^{1}H\}$

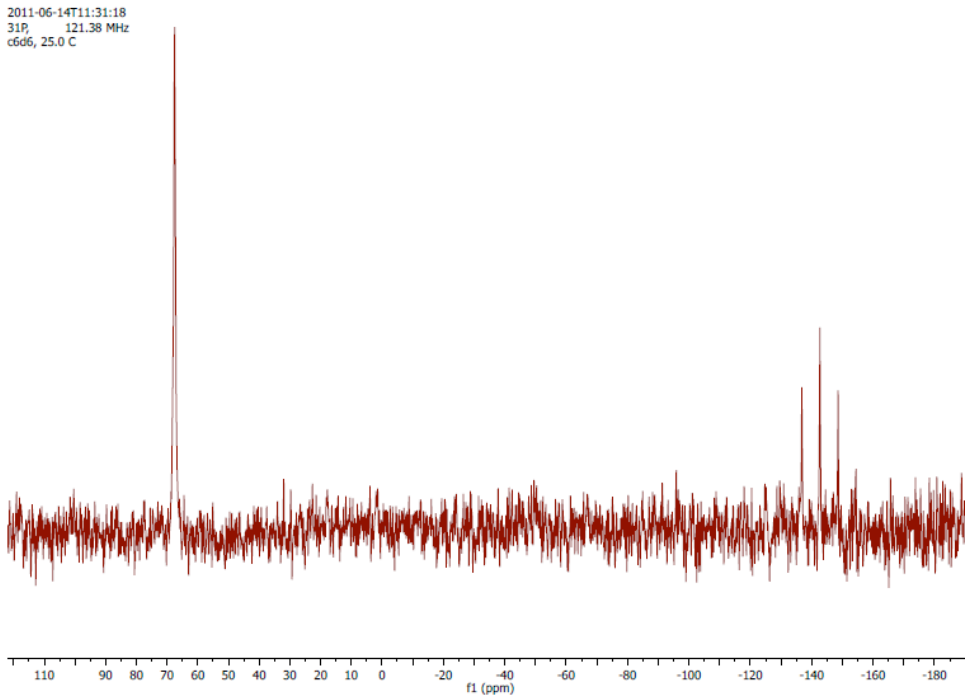
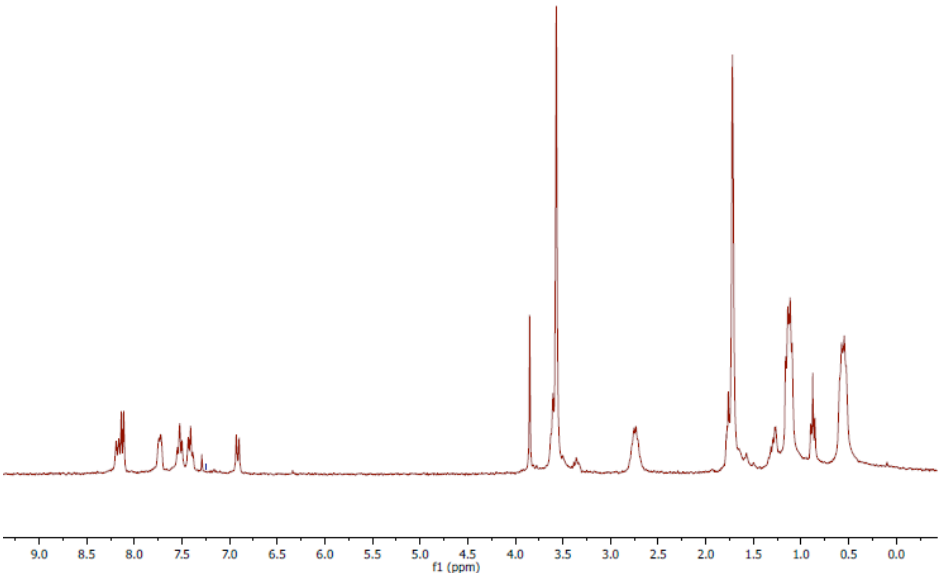
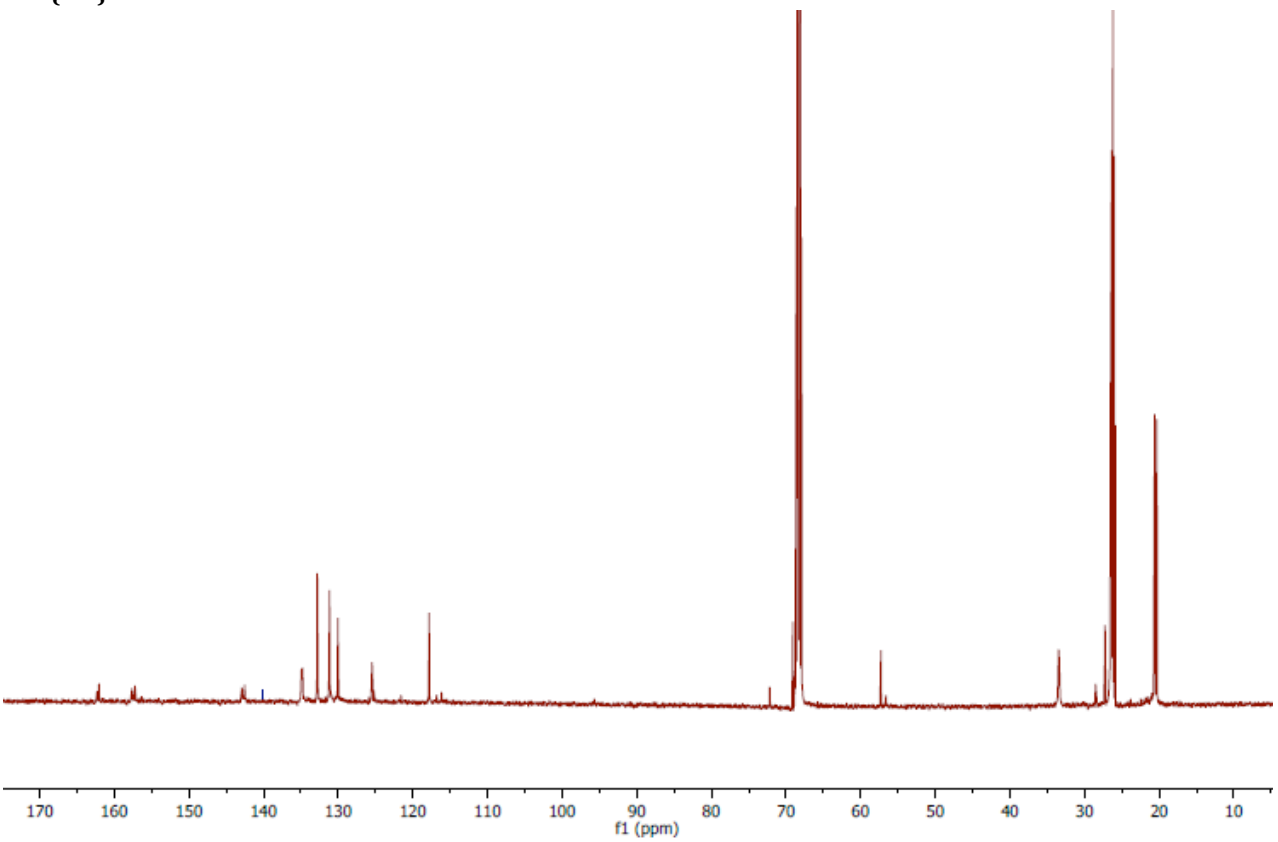

2011-06-14T11:31:18
31P, 121.38 MHz
c6d6, 25.0 C
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)

Figure 17. NMR spectra of {[SiP$^{i\mathrm{Pr}}_3$]Ru(NAr)}PF_6 (Ar = C_6H_4OMe) (7-OMe).

^1H



$^{13}C\{^1H\}$



$^{31}P\{^{1}H\}$

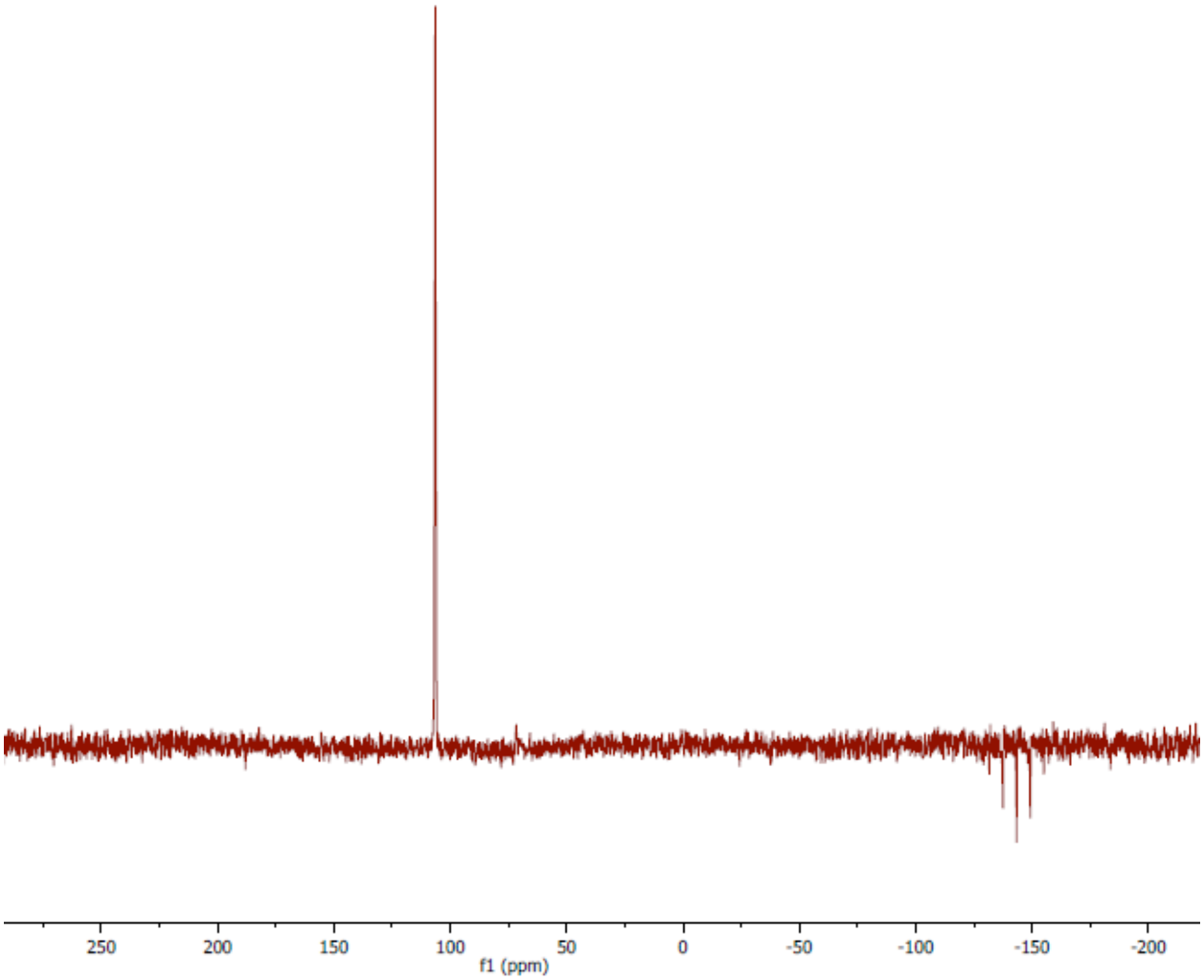
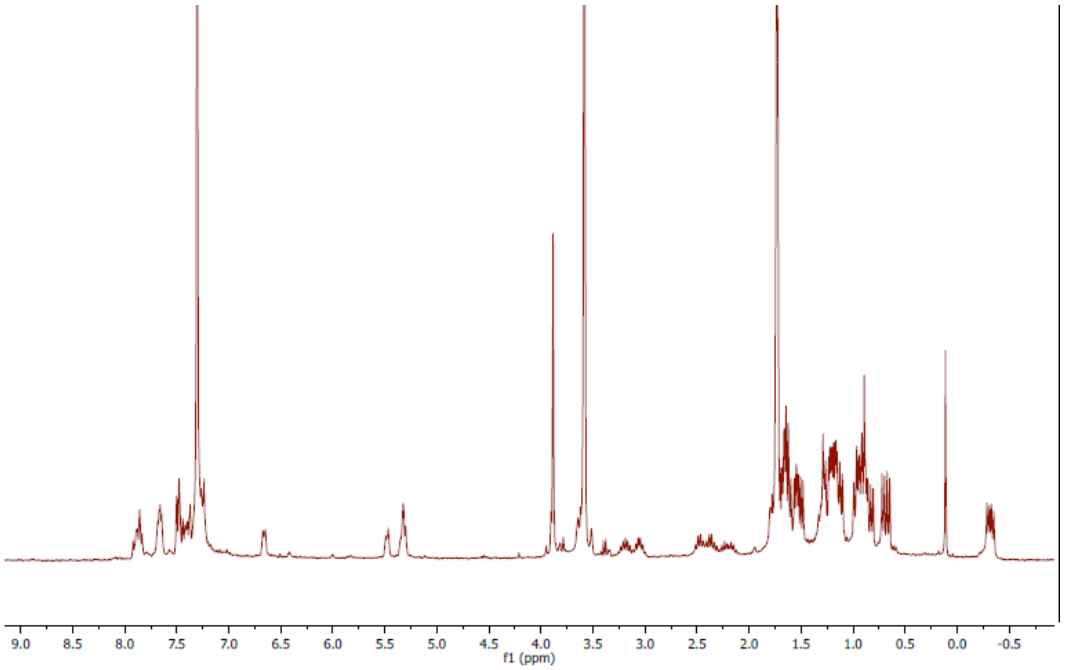
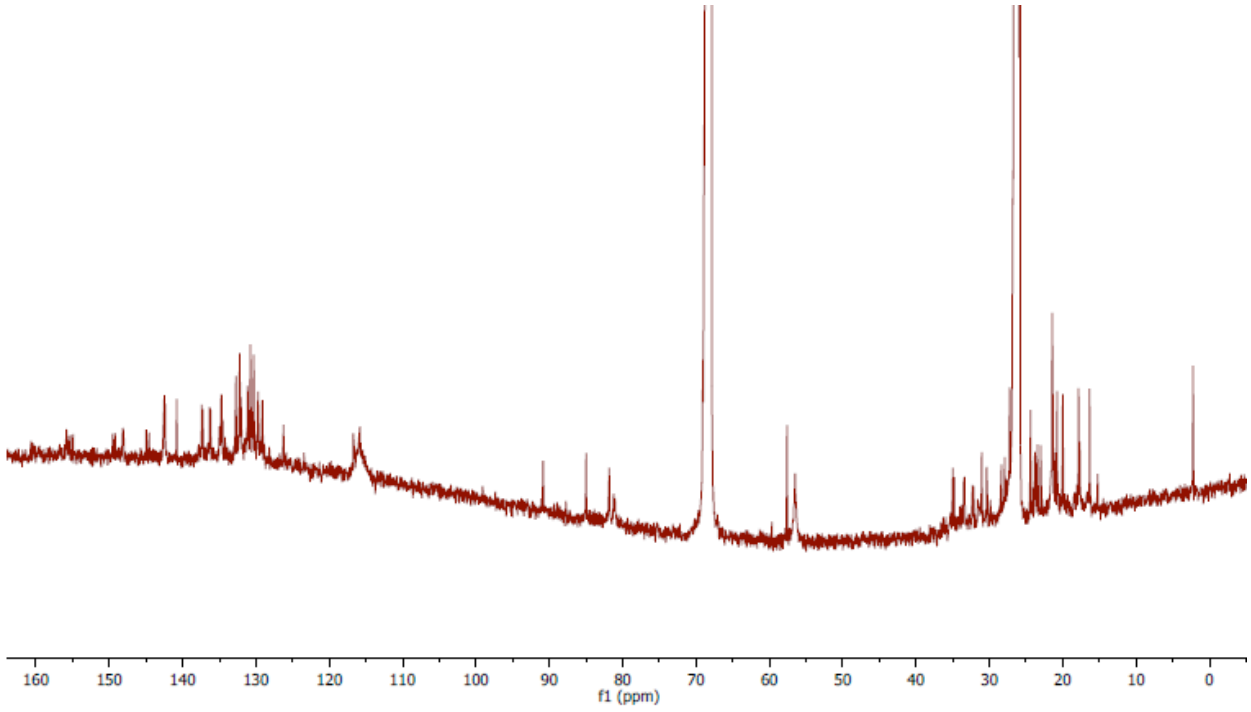


Figure 18. NMR spectra of {[SiP$^{i\mathrm{Pr}}_2$P$^{i\mathrm{Pr}}$(=NAr)]Ru}PF_6 (10).

^{1}H



^{13}C{^{1}H}



$^{31}P\{^{1}H\}$

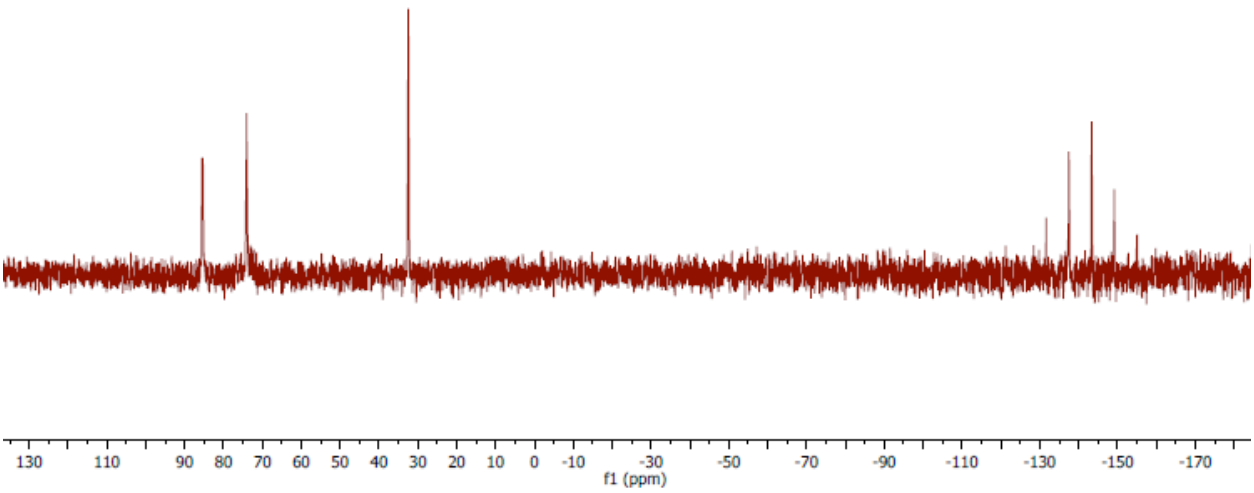

130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
f1 (ppm)

Figure 19. ^{1}H NMR spectrum of [SiP$^{iPr}_{3}$]Ru(NAr) (Ar = C_6H_4OMe) (5-OMe).

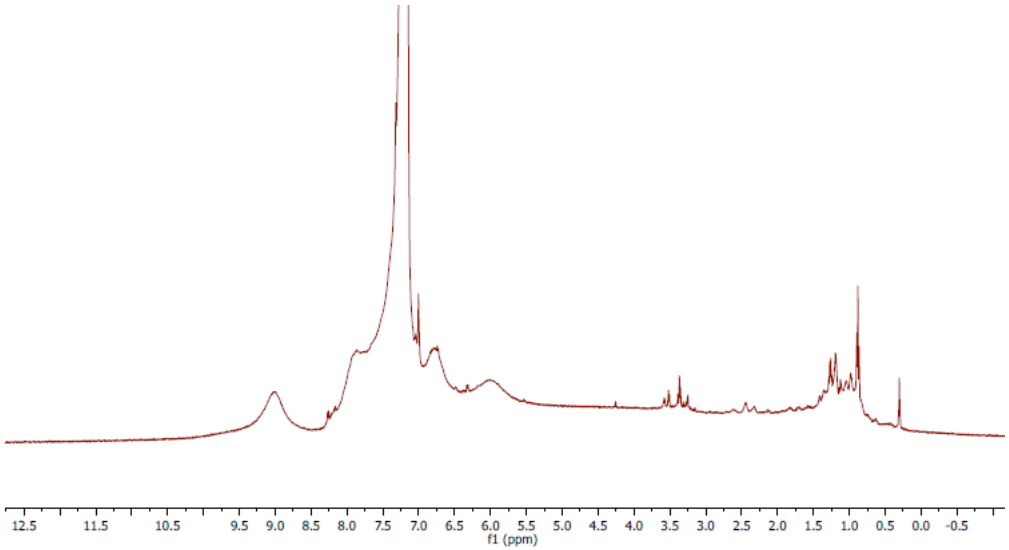
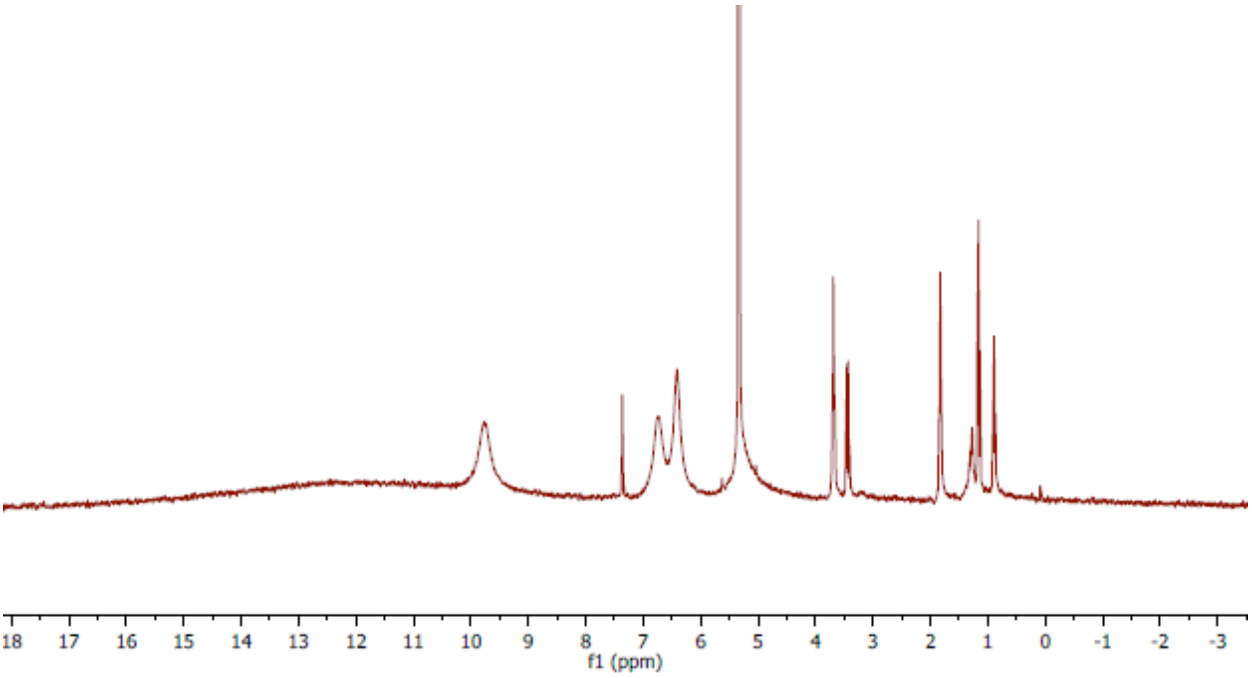


Figure 20. ^{1}H NMR spectrum of {[SiP$^{iPr}_{3}$]RuCl}PF_6 (12).



Details of DFT Calculations.

Computational details: Geometry optimization were run on the Gaussian03[1] suite of programs with the B3LYP[2] level of theory with the LANL2TZ(f)[3] basis set for Ru, the 6-31G(d)[4] basis set for Si, P, and N atoms, and the LANL2DZ[5] basis set for C, O, F and H atoms (hereafter referred to as BS1). Additional energy calculations were run using the same functional as the optimizations with the LANL2TZ(f) for the transition metals, and 6-311G(d,p)[6] basis set for all other atoms (hereafter referred to as BS2). Free enthalpies were calculated at T = 298K using frequency calculations at the B3LYP/BS1 level. Transition state optimizations were carried out using the quadratic synchronous transit (QST3) method[7] as implemented in Gaussian03. A frequency calculation was used to check for the existence of a single imaginary frequency corresponding to the transitional mode. An energy calculation on **7-OMe** starting from its X-ray coordinates was run using the same method and basis set as the above energy calculations.

Results and discussion

The potential energy surface (PES) for nitrene release from [SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar) (Ar = C$_6$H$_4$OMe) (**11-OMe**) was investigated by DFT methods (Figure 21). Five different binding modes of the azide ligand were identified as discussed in the main text (Figure 22). While maintaining the bulky isopropyl groups in the model appears to be important for a realistic energy ordering of the different binding modes, optimizing reaction pathways would require the consideration of the large conformational space arising from rotations around P-C(*i*Pr) bonds. Thus, we turned to the truncated model [SiP$^{Me}_3$]Ru(N$_3$Ph) (Figures 23 & 24). The energy ordering and electronic structures of isomers **A-E** is well reproduced in the truncated system except for the charge-transfer structure **B** and its stereoisomer **B'**, which are additionally stabilized by interaction of the α-Nitrogen atom with the Ru center and thus found at slightly lower energies than the γ-bound structure **A**. Such metallacyclic structures are unlikely to be accessible with isopropyl substituents on the ligand and were not considered further. To locate the transition state for nitrene release from structure **A**, a relaxed PES scan was performed using the N$^{\alpha}$-N$^{\beta}$ distance as the driving coordinate. The obtained maximum energy structure was then used as a starting point for transition state optimization using the QST3 method.

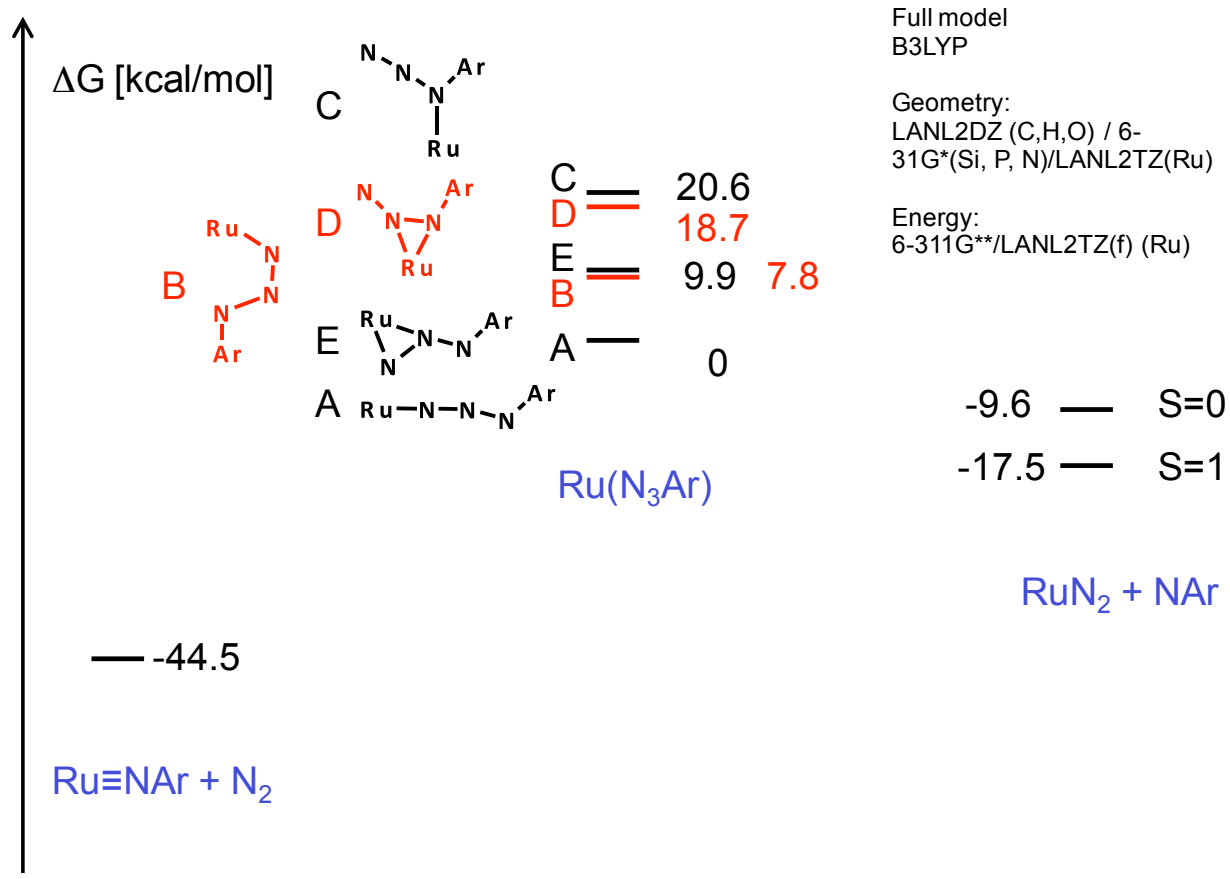


Figure 21. Calculated Potential Energy Surface for [SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar) (Ar = C$_6$H$_4$OMe) (11-OMe). The structures depicted in red have mostly ligand-centered radical character.

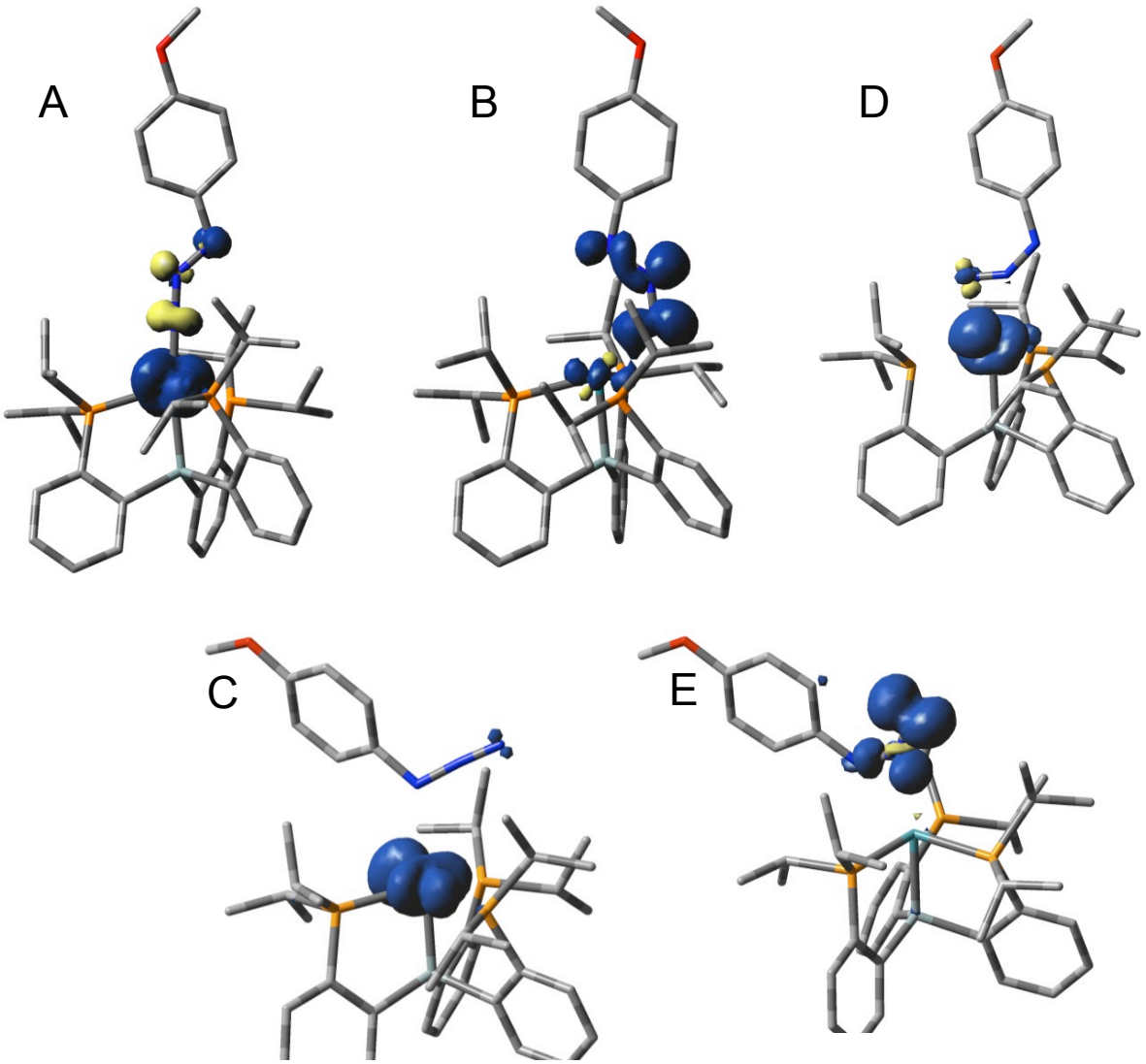


Figure 22. DFT optimized structure and calculated spin density isosurface of azide adducts [SiP$^{iPr}_3$]Ru(N_3Ar) (Ar = C_6H_4OMe) (11-OMe).

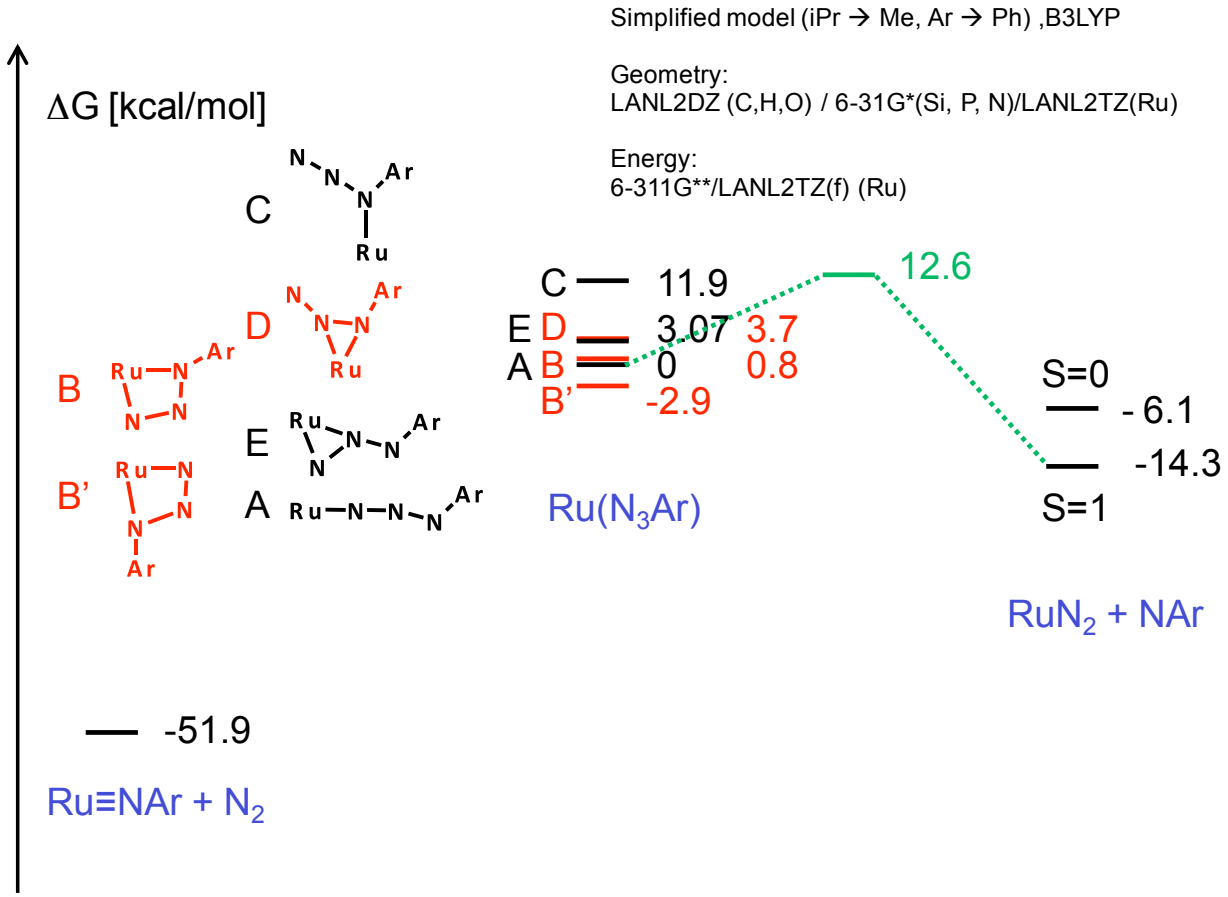


Figure 23. Calculated Potential Energy Surface for the truncated model [SiP$^{Me}_3$]Ru(N$_3$Ph). The structures depicted in red have mostly ligand-centered radical character. The optimized transition state is depicted in green.

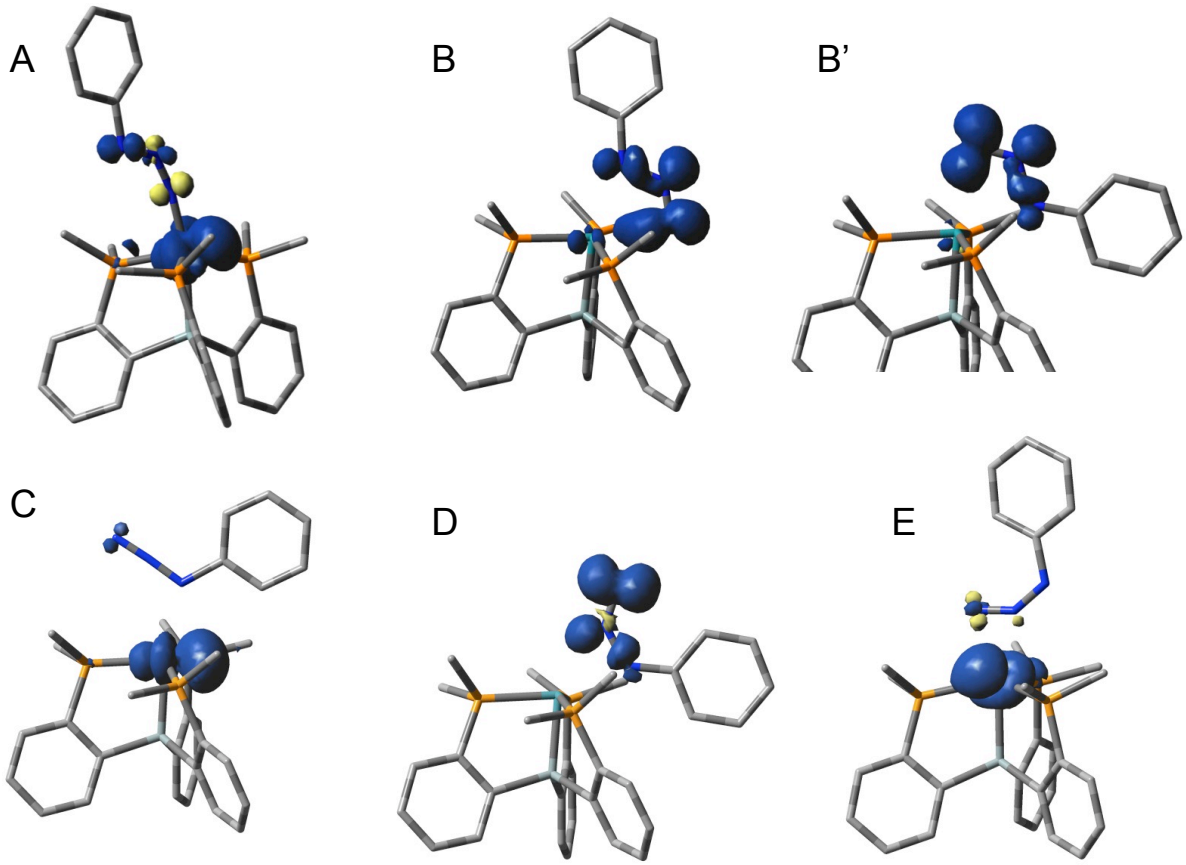


Figure 24. DFT optimized structure and calculated spin density isosurface of azide adducts [SiP$^{Me}_3$]Ru(N$_3$Ph).

Table 5. DFT optimized coordinates of γ-bound azide adduct A, [SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar) (Ar = C$_6$H$_4$OMe) (11-OMe).

Ru	-0.153974	0.203551	-0.100873
Si	-2.523141	-0.177653	-0.017141
P	-0.502845	-1.425570	-1.884255
P	-0.358877	-0.869265	2.081444
P	-0.995985	2.470239	-0.169713
O	9.255831	1.111878	-0.023372
N	1.778993	0.260050	-0.123079
N	2.975716	0.268469	-0.139428
N	3.889926	-0.645884	-0.292656
C	-3.184424	-0.696089	-1.729743
C	-4.509973	-0.541657	-2.196263
H	-5.276951	-0.153011	-1.528519
C	-4.853645	-0.835250	-3.529594
H	-5.875704	-0.694865	-3.875190
C	-3.862407	-1.287619	-4.421111
H	-4.113056	-1.496006	-5.459021
C	-2.540506	-1.466909	-3.970885
H	-1.791801	-1.810130	-4.680157
C	-2.193638	-1.180651	-2.631223
C	-2.891508	-1.612255	1.190810
C	-4.094037	-2.359876	1.189323
H	-4.883734	-2.107881	0.483073
C	-4.284706	-3.447574	2.060857
H	-5.212338	-4.015373	2.033865
C	-3.262833	-3.800920	2.961849
H	-3.396212	-4.640947	3.640122
C	-2.061930	-3.068146	2.987106
H	-1.294943	-3.357330	3.695192
C	-1.855325	-1.983307	2.101704
C	-3.475899	1.399882	0.499040
C	-4.815665	1.444212	0.951303
H	-5.391774	0.523333	1.027250
C	-5.415681	2.655921	1.342655
H	-6.443148	2.666341	1.700303
C	-4.676837	3.853949	1.284801
H	-5.130821	4.792118	1.596332
C	-3.344721	3.834767	0.831638
H	-2.784573	4.766526	0.808101
C	-2.739659	2.618880	0.439442
C	-0.612136	-3.301695	-1.562667
H	-1.562171	-3.388081	-1.012661
C	-0.729703	-4.172478	-2.838840
H	0.193009	-4.154070	-3.431803
H	-1.562931	-3.865137	-3.478301
H	-0.907854	-5.216870	-2.546313
C	0.503260	-3.844310	-0.640090
H	0.352981	-4.922043	-0.483841

H	0.475969	-3.359482	0.336308
H	1.504038	-3.702275	-1.061274
C	0.660314	-1.254247	-3.359940
H	0.215916	-1.838536	-4.179055
C	0.739239	0.224427	-3.811713
H	1.190531	0.843446	-3.026406
H	-0.247220	0.637294	-4.052830
H	1.368422	0.302884	-4.709236
C	2.077787	-1.819164	-3.098621
H	2.728767	-1.564399	-3.946880
H	2.075572	-2.911007	-3.005348
H	2.539760	-1.405577	-2.195984
C	-0.631193	0.085776	3.710073
H	0.193421	0.812254	3.730831
C	-1.966180	0.865604	3.698948
H	-2.821685	0.179750	3.722220
H	-2.072459	1.503114	2.820673
H	-2.024781	1.504091	4.591825
C	-0.564868	-0.750264	5.014192
H	-0.659935	-0.073696	5.875946
H	0.373463	-1.298666	5.129668
H	-1.395391	-1.463282	5.068237
C	1.262488	-1.827179	2.405593
H	1.610326	-2.016441	1.384475
C	1.242503	-3.193490	3.133636
H	2.264511	-3.599148	3.136769
H	0.603093	-3.922878	2.625055
H	0.919071	-3.117960	4.177908
C	2.318993	-0.882175	3.042376
H	2.132120	-0.706043	4.107727
H	2.362250	0.085485	2.531043
H	3.310776	-1.342228	2.947988
C	-1.066332	3.254532	-1.908473
H	-0.085100	3.007176	-2.341401
C	-1.248288	4.793056	-1.952752
H	-1.279913	5.117559	-3.002448
H	-0.433074	5.340367	-1.468258
H	-2.197060	5.094678	-1.491514
C	-2.158044	2.596909	-2.785068
H	-3.160934	2.841721	-2.413584
H	-2.069755	1.509647	-2.819824
H	-2.079738	2.977972	-3.812910
C	-0.024895	3.787325	0.772710
H	-0.530038	4.747570	0.594720
C	0.003716	3.548194	2.297195
H	0.498560	2.599935	2.533155
H	-1.000731	3.532849	2.733264
H	0.570936	4.354234	2.783675
C	1.419439	3.880860	0.220914

H	1.970021	4.666152	0.757109
H	1.450183	4.123610	-0.847857
H	1.949986	2.933208	0.366213
C	5.208279	-0.150118	-0.217156
C	5.575660	1.208199	-0.007714
H	4.797769	1.958669	0.105970
C	6.921158	1.586563	0.050344
H	7.206932	2.622819	0.209027
C	7.940778	0.622557	-0.098215
C	7.597854	-0.728616	-0.306617
H	8.362322	-1.490755	-0.424834
C	6.243346	-1.102367	-0.364472
H	5.970303	-2.142114	-0.526134
C	10.348308	0.165509	-0.169217
H	10.326353	-0.597898	0.622186
H	11.261391	0.758606	-0.080037
H	10.323847	-0.327506	-1.152036

Table 6. DFT optimized coordinates of γ-bound azide adduct B, [SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar) (Ar = C$_6$H$_4$OMe) (11-OMe).

Ru	-0.092741	0.001353	-0.046072
Si	-2.327768	0.338286	-0.456173
P	-0.745658	-2.291469	-0.852720
P	-0.904940	-0.167931	2.134173
P	0.062638	2.359291	-0.560078
N	2.695639	-0.180513	-1.175503
N	1.517161	-0.146654	-1.437449
C	-2.800845	-0.695122	-1.970224
C	-3.802316	-0.373670	-2.916133
H	-4.349112	0.563365	-2.824436
C	-4.091036	-1.231037	-3.993028
H	-4.855699	-0.961970	-4.718565
C	-3.380855	-2.439626	-4.127459
H	-3.597223	-3.114005	-4.952944
C	-2.381973	-2.774845	-3.196441
H	-1.852860	-3.715432	-3.320152
C	-2.069590	-1.910260	-2.121564
C	-3.388938	-0.373054	0.975915
C	-4.773967	-0.654317	0.906623
H	-5.320461	-0.459796	-0.015049
C	-5.461652	-1.207489	2.002581
H	-6.525361	-1.423432	1.928445
C	-4.765665	-1.487719	3.195032
H	-5.289949	-1.916818	4.046084
C	-3.387884	-1.217084	3.286182
H	-2.872235	-1.442349	4.213460
C	-2.691485	-0.672414	2.181980
C	-2.734284	2.193731	-0.623971
C	-4.046554	2.719289	-0.698730
H	-4.899666	2.043497	-0.733866
C	-4.283285	4.106359	-0.696223
H	-5.300865	4.487441	-0.747122
C	-3.197301	4.997933	-0.609089

H	-3.370175	6.071722	-0.591831
C	-1.883433	4.498448	-0.542818
H	-1.059090	5.203410	-0.474325
C	-1.638826	3.106081	-0.552971
C	-1.649619	-3.579633	0.249743
H	-2.152571	-2.954200	0.997820
C	-2.747245	-4.411806	-0.460434
H	-2.332529	-5.036065	-1.263240
H	-3.534630	-3.785624	-0.887467
H	-3.212167	-5.086722	0.272567
C	-0.710514	-4.559292	1.001566
H	-1.300622	-5.116213	1.742669
H	0.105146	-4.063051	1.534651
H	-0.271289	-5.293778	0.315778
C	0.508878	-3.350223	-1.808756
H	0.017856	-4.325462	-1.967166
C	0.906661	-2.776250	-3.195268
H	1.438069	-1.828607	-3.079756
H	0.051380	-2.606090	-3.854262
H	1.578943	-3.490746	-3.691588
C	1.801258	-3.584875	-0.978689
H	2.512890	-4.164233	-1.583239
H	1.624898	-4.143144	-0.056136
H	2.284268	-2.639545	-0.715045
C	-0.891593	1.273224	3.367909
H	0.087435	1.740818	3.209926
C	-1.993283	2.309592	3.034670
H	-2.987782	1.904994	3.257685
H	-1.985823	2.619493	1.988252
H	-1.849498	3.205599	3.654192
C	-1.001833	0.905436	4.870039
H	-0.977847	1.832902	5.459748
H	-0.179873	0.275305	5.219544
H	-1.950427	0.404650	5.096172
C	0.217240	-1.488617	2.898517
H	0.378058	-2.152666	2.041593
C	-0.309792	-2.373541	4.054305
H	0.464443	-3.110812	4.311469
H	-1.207485	-2.930007	3.763877
H	-0.533631	-1.806060	4.962768
C	1.607528	-0.870087	3.215450
H	1.568668	-0.149372	4.040867
H	2.040592	-0.382514	2.333495
H	2.296746	-1.673161	3.511380
C	0.531221	2.555290	-2.400326
H	1.516464	2.077435	-2.465434
C	0.647010	4.015307	-2.903024
H	0.911697	4.000365	-3.969612
H	1.424154	4.589495	-2.386708
H	-0.305214	4.552276	-2.811359
C	-0.423119	1.766663	-3.327161
H	-1.439320	2.179949	-3.306748
H	-0.470543	0.709660	-3.056939
H	-0.056689	1.833256	-4.361245
C	1.198177	3.658489	0.209887
H	1.007331	4.598356	-0.326472

C	0.944479	3.919690	1.709815
H	1.259182	3.059035	2.309727
H	-0.105301	4.139107	1.931486
H	1.545218	4.780532	2.035027
C	2.681772	3.265844	-0.011356
H	3.332182	4.003358	0.478739
H	2.956475	3.236262	-1.071787
H	2.904469	2.280663	0.415852
N	3.330697	-0.290464	-0.025949
C	4.734926	-0.269534	-0.151183
C	5.459066	-0.119644	-1.368276
C	5.481833	-0.403804	1.043427
C	6.858684	-0.106393	-1.377197
H	4.912249	-0.017853	-2.301606
C	6.888941	-0.389762	1.041330
H	4.942250	-0.521813	1.980292
C	7.583588	-0.240206	-0.175038
H	7.411647	0.006425	-2.306061
H	7.420192	-0.496192	1.982834
O	8.986297	-0.211972	-0.300401
C	9.780535	-0.350312	0.906321
H	9.595307	-1.314952	1.401941
H	10.821806	-0.302122	0.578591
H	9.580348	0.466178	1.616124

Table 7. DFT optimized coordinates of α -bound azide adduct C, [SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar) (Ar = C$_6$H$_4$OMe) (11-OMe).

Ru	-0.071564	-0.164751	-0.195077
Si	1.796941	0.712670	0.814207
P	0.573030	-2.041019	1.271889
P	1.472275	-0.280718	-2.084903
P	-0.851572	2.117706	0.035885
N	-2.057881	-2.270529	-1.715468
N	-1.807338	-3.201166	-2.327088
C	2.029291	-0.000632	2.563109
C	2.691549	0.618827	3.649627
H	3.090670	1.624995	3.533460
C	2.822595	-0.028203	4.891952
H	3.322191	0.469885	5.720581
C	2.299083	-1.325286	5.056839
H	2.396538	-1.839762	6.010620
C	1.639214	-1.956034	3.986925
H	1.242675	-2.955770	4.142821
C	1.483625	-1.302996	2.741065
C	3.378944	0.138024	-0.107502
C	4.676239	0.159554	0.459789
H	4.815401	0.547856	1.467626
C	5.792525	-0.340526	-0.234490
H	6.778452	-0.322327	0.225682
C	5.621698	-0.872876	-1.526311
H	6.475224	-1.265077	-2.075630

C	4.342873	-0.899047	-2.112643
H	4.243657	-1.306131	-3.111236
C	3.211635	-0.410829	-1.414258
C	1.777657	2.621017	0.884794
C	2.877371	3.436641	1.244918
H	3.818148	2.974924	1.540726
C	2.799387	4.840403	1.193718
H	3.660556	5.447401	1.465628
C	1.605180	5.454895	0.770465
H	1.536611	6.539345	0.714150
C	0.498674	4.663300	0.412023
H	-0.408172	5.160095	0.077528
C	0.569282	3.251162	0.467304
C	1.868034	-3.320974	0.675470
H	2.584199	-2.672351	0.151608
C	2.650705	-4.094811	1.764040
H	1.987783	-4.718493	2.380244
H	3.209730	-3.427794	2.425527
H	3.372165	-4.769109	1.279440
C	1.307733	-4.335942	-0.354161
H	2.136886	-4.771151	-0.929435
H	0.609216	-3.884146	-1.065037
H	0.793121	-5.164433	0.148784
C	-0.713755	-3.117232	2.182400
H	-0.143054	-3.874116	2.743507
C	-1.550314	-2.292400	3.193286
H	-2.102747	-1.497713	2.677938
H	-0.939176	-1.824356	3.969209
H	-2.286166	-2.946041	3.683722
C	-1.690263	-3.865720	1.240430
H	-2.292749	-4.572728	1.828979
H	-1.189821	-4.432593	0.452756
H	-2.383893	-3.160749	0.770899
C	1.761137	1.110828	-3.371429
H	0.753646	1.324695	-3.756389
C	2.304769	2.391284	-2.695131
H	3.341838	2.247778	-2.368758
H	1.720058	2.687355	-1.824079
H	2.291074	3.223186	-3.413885
C	2.675618	0.786239	-4.580912
H	2.697393	1.655879	-5.254622
H	2.337490	-0.072482	-5.166872
H	3.706396	0.602608	-4.257421
C	1.063659	-1.779597	-3.189782
H	0.575234	-2.444027	-2.467706
C	2.166224	-2.638793	-3.856879
H	1.688705	-3.487034	-4.370301
H	2.859218	-3.052497	-3.116781
H	2.746150	-2.088150	-4.605295

C	-0.022543	-1.378997	-4.227182
H	0.399976	-0.813854	-5.064713
H	-0.813551	-0.767000	-3.774070
H	-0.489834	-2.283645	-4.637736
C	-1.964856	2.342680	1.580937
H	-2.839991	1.715930	1.360143
C	-2.477326	3.774206	1.874743
H	-3.106872	3.755187	2.776682
H	-3.086115	4.186705	1.061808
H	-1.646479	4.461719	2.071326
C	-1.274119	1.775357	2.843470
H	-0.410825	2.389505	3.128673
H	-0.914838	0.753665	2.686091
H	-1.977658	1.773809	3.689110
C	-1.844686	3.148146	-1.215214
H	-2.039078	4.128352	-0.758174
C	-1.084380	3.390097	-2.536454
H	-0.866261	2.439643	-3.036348
H	-0.140039	3.921418	-2.382450
H	-1.704905	3.992396	-3.215814
C	-3.208995	2.484561	-1.517145
H	-3.774518	3.103297	-2.228345
H	-3.828531	2.356135	-0.622239
H	-3.067028	1.497281	-1.971923
N	-2.246222	-1.257816	-1.013850
C	-3.654555	-1.001618	-0.773077
C	-4.630514	-1.187702	-1.778551
C	-4.039688	-0.541085	0.492813
C	-5.975399	-0.912389	-1.509131
H	-4.342723	-1.535371	-2.768148
C	-5.389410	-0.259921	0.770520
H	-3.283071	-0.415375	1.258373
C	-6.361835	-0.445731	-0.233497
H	-6.740579	-1.045755	-2.267639
H	-5.663112	0.090419	1.760473
O	-7.725499	-0.200864	-0.072484
C	-8.201457	0.283904	1.216500
H	-7.748131	1.252613	1.468855
H	-9.280117	0.402553	1.098580
H	-7.994276	-0.441694	2.015280

Table 8. DFT optimized coordinates of (α,β)-N η^2-bound azide adduct D, [SiP^{iPr}_3]Ru(N_3Ar) (Ar = C_6H_4OMe) (11-OMe).

Ru	0.037963	0.040541	-0.523882
Si	1.446582	0.235193	1.307733
P	0.321976	-2.389307	0.166460
P	2.064291	0.262706	-1.672576
P	-0.575027	2.260263	0.150511
N	-1.634280	-0.273527	-2.049917
N	-2.008278	-0.251533	-3.202644
C	1.016932	-1.090347	2.592566
C	1.170264	-0.992626	3.995432
H	1.525488	-0.061385	4.433857
C	0.852297	-2.069740	4.842458
H	0.963237	-1.971744	5.920365
C	0.390883	-3.277481	4.284493
H	0.149704	-4.121999	4.926232
C	0.234161	-3.392902	2.891767
H	-0.116101	-4.338389	2.487990
C	0.523111	-2.306431	2.032942
C	3.237013	-0.216448	0.782795
C	4.281929	-0.538738	1.681639
H	4.093125	-0.526024	2.754082
C	5.559574	-0.903385	1.220395
H	6.346868	-1.154236	1.928193
C	5.811631	-0.950232	-0.164631
H	6.794948	-1.234056	-0.533330
C	4.788805	-0.633601	-1.076695
H	5.008143	-0.680761	-2.136999
C	3.498623	-0.276343	-0.616433
C	1.511882	2.017890	1.991173
C	2.408043	2.485535	2.981496
H	3.079203	1.786539	3.478026
C	2.479061	3.849184	3.322443
H	3.181119	4.187021	4.081721
C	1.651088	4.777329	2.662336
H	1.709957	5.835386	2.908164
C	0.744831	4.334781	1.680877
H	0.114479	5.066408	1.181872
C	0.664383	2.964947	1.342165
C	1.867452	-3.423356	-0.322412
H	2.642874	-2.661668	-0.461553
C	2.388801	-4.407227	0.754972
H	1.653476	-5.188894	0.989042
H	2.657912	-3.901403	1.685600
H	3.288576	-4.909468	0.371185
C	1.718495	-4.199181	-1.657192
H	2.700924	-4.597090	-1.947313
H	1.356896	-3.579886	-2.482468

H	1.040323	-5.054063	-1.548965
C	-1.072696	-3.664343	-0.062164
H	-0.613802	-4.634062	0.193652
C	-2.308912	-3.457043	0.847063
H	-2.862589	-2.569733	0.538848
H	-2.063060	-3.357343	1.906956
H	-2.980190	-4.320918	0.735555
C	-1.574019	-3.732688	-1.530679
H	-2.279955	-4.569758	-1.628214
H	-0.778562	-3.884014	-2.262996
H	-2.106878	-2.815592	-1.793372
C	2.749732	1.905488	-2.343466
H	1.896098	2.357538	-2.862859
C	3.198521	2.849149	-1.201632
H	4.099114	2.461466	-0.710746
H	2.436813	2.988792	-0.434769
H	3.443643	3.835622	-1.619489
C	3.919863	1.802681	-3.357425
H	4.159729	2.814379	-3.714775
H	3.688571	1.193718	-4.234032
H	4.824516	1.406620	-2.883132
C	1.877655	-0.828897	-3.218633
H	1.162774	-1.578408	-2.859474
C	3.106586	-1.596775	-3.764434
H	2.774936	-2.247127	-4.586786
H	3.565356	-2.236655	-3.004272
H	3.877674	-0.931682	-4.167699
C	1.150383	-0.058628	-4.354660
H	1.794984	0.686236	-4.833909
H	0.240181	0.432673	-3.998518
H	0.841597	-0.774694	-5.128208
C	-2.099478	2.166225	1.293576
H	-2.866937	1.691829	0.673551
C	-2.650705	3.528226	1.785496
H	-3.501800	3.341070	2.455237
H	-3.017080	4.163328	0.971802
H	-1.900684	4.087331	2.358227
C	-1.847950	1.253594	2.516683
H	-1.108276	1.691970	3.197341
H	-1.494383	0.260793	2.226065
H	-2.785311	1.133297	3.077891
C	-1.100619	3.695962	-0.963003
H	-1.387795	4.521609	-0.297459
C	0.002820	4.221169	-1.905020
H	0.255957	3.469319	-2.659849
H	0.916114	4.505341	-1.372343
H	-0.366688	5.108567	-2.438046
C	-2.344732	3.290151	-1.795289
H	-2.659410	4.137804	-2.419888

H	-3.199199	3.001166	-1.173839
H	-2.116931	2.450689	-2.462529
N	-2.233891	-0.371460	-0.861613
C	-3.643016	-0.345297	-0.787283
C	-4.524190	-0.234498	-1.901745
C	-4.229663	-0.452133	0.501068
C	-5.914422	-0.229812	-1.719560
H	-4.122790	-0.156718	-2.905122
C	-5.620829	-0.447751	0.684243
H	-3.580538	-0.546518	1.365223
C	-6.474378	-0.335271	-0.432795
H	-6.582760	-0.146730	-2.572118
H	-6.019173	-0.535923	1.690697
O	-7.877469	-0.320253	-0.369817
C	-8.507839	-0.441388	0.933487
H	-8.228187	0.392283	1.594270
H	-9.582665	-0.410233	0.741076
H	-8.248024	-1.393829	1.418275

Table 9. DFT optimized coordinates of (β,γ)-N η^2-bound azide adduct E, [SiP$^{i\mathrm{Pr}}_3$]Ru(N$_3$Ar) (Ar = C$_6$H$_4$OMe) (11-OMe).

Ru	0.047534	-0.185402	-0.197971
Si	-2.310867	0.078066	0.220060
P	-0.028357	0.382073	2.228762
P	-0.484363	1.849514	-1.473998
P	-0.860769	-2.316318	-0.981698
N	2.128994	-0.001492	-0.103216
N	3.138018	0.806052	-0.165610
C	-2.735560	-0.244517	2.048498
C	-4.011430	-0.615826	2.535908
H	-4.836330	-0.758768	1.840312
C	-4.228886	-0.846511	3.906106
H	-5.212296	-1.146856	4.261633
C	-3.162327	-0.700631	4.814894
H	-3.317360	-0.883691	5.875908
C	-1.890022	-0.325406	4.348622
H	-1.081889	-0.223414	5.067800
C	-1.665071	-0.099950	2.970526
C	-2.875018	1.876620	-0.091120
C	-4.090330	2.418966	0.392667
H	-4.767796	1.794665	0.972486
C	-4.430113	3.765335	0.171370
H	-5.363208	4.165845	0.561718
C	-3.550375	4.593656	-0.551269
H	-3.801828	5.636958	-0.729091
C	-2.340092	4.074482	-1.045197
H	-1.685428	4.730880	-1.604955
C	-1.984346	2.724653	-0.810023
C	-3.369090	-1.138015	-0.805174
C	-4.756119	-1.015794	-1.057124
H	-5.304618	-0.159361	-0.668787
C	-5.442361	-1.965627	-1.836297

H	-6.506571	-1.847604	-2.029026
C	-4.744748	-3.062914	-2.378567
H	-5.267407	-3.795904	-2.989099
C	-3.365749	-3.204518	-2.138414
H	-2.840484	-4.048167	-2.579033
C	-2.673522	-2.250271	-1.357886
C	0.019124	2.240360	2.637239
H	-0.754759	2.629191	1.958520
C	-0.382672	2.633679	4.079865
H	0.311324	2.215682	4.821978
H	-1.397123	2.312022	4.333185
H	-0.342795	3.727982	4.178811
C	1.364687	2.924323	2.267422
H	1.183880	3.978875	2.016848
H	1.874985	2.451300	1.423423
H	2.053218	2.910155	3.121125
C	1.189133	-0.425955	3.435886
H	0.908737	-0.039975	4.428997
C	1.021227	-1.966048	3.445320
H	1.268796	-2.378980	2.461038
H	0.007493	-2.279444	3.713566
H	1.714502	-2.401238	4.178812
C	2.683124	-0.084315	3.212030
H	3.266907	-0.515682	4.038051
H	2.885011	0.988068	3.187556
H	3.055726	-0.522665	2.283547
C	-0.964643	1.719088	-3.312972
H	-0.140927	1.147773	-3.764781
C	-2.276173	0.924324	-3.508471
H	-3.136238	1.487877	-3.127220
H	-2.259719	-0.042116	-3.004144
H	-2.440902	0.746949	-4.580624
C	-1.095068	3.065816	-4.070980
H	-1.275853	2.859236	-5.135750
H	-0.201252	3.690948	-4.004156
H	-1.951295	3.641934	-3.701750
C	1.049861	2.969351	-1.484544
H	1.556481	2.666999	-0.563951
C	0.891168	4.507453	-1.424469
H	1.892297	4.953550	-1.335497
H	0.312312	4.826801	-0.550920
H	0.426703	4.929176	-2.323729
C	2.014963	2.551872	-2.627226
H	1.674838	2.888654	-3.612961
H	2.167172	1.467595	-2.653126
H	2.997929	3.000498	-2.436821
C	-0.684284	-3.794699	0.192197
H	0.363534	-3.731173	0.521405
C	-0.925157	-5.193805	-0.428563
H	-0.766672	-5.957883	0.345558
H	-0.246737	-5.423795	-1.256313
H	-1.958406	-5.300397	-0.781954
C	-1.596122	-3.628791	1.430286
H	-2.653947	-3.727170	1.155872
H	-1.461686	-2.660539	1.914545
H	-1.364285	-4.412010	2.165047

C	-0.091870	-2.994821	-2.570861
H	-0.651795	-3.912034	-2.807230
C	-0.248061	-2.030741	-3.767131
H	0.270914	-1.084337	-3.575033
H	-1.297407	-1.812352	-3.990768
H	0.200625	-2.484056	-4.662075
C	1.399050	-3.371481	-2.386573
H	1.778466	-3.812007	-3.319372
H	1.558074	-4.098654	-1.582442
H	2.000653	-2.489214	-2.148794
N	1.902231	-1.218572	0.005718
C	4.435175	0.237825	-0.156018
C	5.492943	1.181198	-0.193958
C	4.777804	-1.143468	-0.125457
C	6.838495	0.784568	-0.200335
H	5.234098	2.236964	-0.218405
C	6.122154	-1.544428	-0.134038
H	3.995554	-1.892410	-0.095886
C	7.156916	-0.590783	-0.170472
H	7.616365	1.541843	-0.229526
H	6.388637	-2.597553	-0.111655
O	8.463882	-1.105025	-0.174657
C	9.572350	-0.166232	-0.209831
H	9.569830	0.491443	0.671663
H	10.474943	-0.781582	-0.204342
H	9.550465	0.447051	-1.1224

Table 10. DFT optimized coordinates of singlet nitrene ^{1}ArN (Ar = C_6H_4OMe)

O	-2.159709	0.606594	-0.000027
N	3.307568	-0.358211	0.000097
C	2.013742	-0.157880	-0.000130
C	1.451125	1.191787	0.000017
H	2.137636	2.033298	0.000095
C	0.081992	1.388723	0.000001
H	-0.344822	2.387475	0.000044
C	-0.810958	0.278565	-0.000049
C	-0.303927	-1.047970	-0.000029
H	-0.977285	-1.899691	-0.000003
C	1.070482	-1.269138	-0.000011
H	1.470214	-2.279127	0.000048
C	-3.154669	-0.461439	0.000056
H	-3.063968	-1.085301	-0.899098
H	-4.119976	0.047483	0.000128
H	-3.063828	-1.085295	0.899199

Table 11. DFT optimized coordinates of triplet nitrene ^{1}ArN (Ar = C_6H_4OMe)

Atom	X	Y	Z
O	-2.162423	0.606332	-0.000088
N	3.318191	-0.359494	0.000040
C	2.004294	-0.155725	0.000034
C	1.451542	1.185357	0.000018
H	2.137323	2.027927	0.000015
C	0.078527	1.387082	-0.000007
H	-0.345811	2.386714	-0.000013

C	-0.811962	0.279861	-0.000023
C	-0.305494	-1.043843	-0.000046
H	-0.976917	-1.896873	-0.000101
C	1.073682	-1.261461	-0.000036
H	1.472637	-2.272165	-0.000082
C	-3.152934	-0.464947	0.000092
H	-3.060518	-1.089064	-0.898912
H	-4.120278	0.040268	0.000169
H	-3.060305	-1.088954	0.899152

Table 12. DFT optimized coordinates of γ-N η ^{1}-bound azide adduct A, [SiP$^{Me}_{3}$]Ru(N$_3$Ph).

Ru	-0.248013	-0.572656	-0.285543
Si	1.974977	0.322207	-0.026445
P	-0.563225	1.650855	-1.076770
P	-0.159113	-0.534427	2.062576
P	1.038361	-2.400504	-1.087923
N	-2.172090	-0.831231	-0.348622
N	-3.355623	-0.691088	-0.306081
N	-4.133203	0.294202	0.063101
C	2.215212	1.886660	-1.095134
C	3.444518	2.492157	-1.452302
H	4.384529	2.030038	-1.157152
C	3.481681	3.678623	-2.207870
H	4.437200	4.121913	-2.480193
C	2.280010	4.292104	-2.614925
H	2.304447	5.210745	-3.196775
C	1.047405	3.706510	-2.274619
H	0.126158	4.184869	-2.601592
C	1.011202	2.505874	-1.531182
C	2.246317	0.856571	1.792752
C	3.338098	1.626098	2.266429
H	4.089741	1.989393	1.567519
C	3.464893	1.955891	3.627502
H	4.308492	2.552381	3.968433
C	2.493191	1.518144	4.550505
H	2.586268	1.771196	5.604289
C	1.396674	0.761520	4.102009
H	0.647171	0.439020	4.822327
C	1.266050	0.435321	2.732545
C	3.330337	-0.965457	-0.438998
C	4.728183	-0.787989	-0.285442
H	5.118126	0.146981	0.112401
C	5.636188	-1.809631	-0.615689
H	6.704810	-1.651568	-0.486986
C	5.161459	-3.042602	-1.107705
H	5.860868	-3.835028	-1.364296
C	3.778955	-3.246637	-1.257901
H	3.422882	-4.205406	-1.630354
C	2.867820	-2.219296	-0.923296
C	-1.430053	2.891707	-0.006812
H	-0.874880	3.024554	0.929230
C	-1.593422	1.738392	-2.614683
H	-1.713741	2.770073	-2.970727
C	0.005867	-2.152636	2.963100
H	-0.831591	-2.807409	2.690928

C	-1.631807	0.181924	2.931896
H	-1.750776	1.233874	2.653260
C	0.809404	-2.719554	-2.903730
H	-0.248346	-2.929310	-3.105963
C	0.694998	-4.092468	-0.403437
H	1.275487	-4.873129	-0.912867
C	-5.506893	0.002355	-0.036653
C	-6.063155	-1.226939	-0.482928
H	-5.398521	-2.032903	-0.784177
C	-7.455937	-1.398825	-0.536111
H	-7.863561	-2.347469	-0.881309
C	-8.328366	-0.360440	-0.149391
C	-7.781693	0.861630	0.294307
H	-8.440527	1.673430	0.596668
C	-6.390945	1.043452	0.350681
H	-5.965515	1.983738	0.693239
H	-1.132413	1.139670	-3.407892
H	-2.585705	1.327656	-2.394505
H	-1.547278	0.108455	4.024355
H	-2.533711	-0.350322	2.608361
H	0.942902	-2.641274	2.672371
H	0.007736	-2.013951	4.052686
H	0.931859	-4.117087	0.665557
H	-0.372837	-4.312012	-0.525064
H	1.414872	-3.569400	-3.247395
H	1.099380	-1.826916	-3.468840
H	-1.514555	3.866862	-0.505569
H	-2.431456	2.507699	0.222605
H	-9.405692	-0.500210	-0.192975

Table 13. DFT optimized coordinates of (α,γ)-N κ^3-bound azide adduct B, [SiP$^{Me}_3$]Ru(N$_3$Ph).

Ru	0.564979	-0.046055	-0.096658
Si	-1.743338	0.103265	-0.243850
P	0.028703	-2.373385	-0.288106
P	0.182833	0.135616	2.148154
P	0.494357	2.250627	-0.716515
N	2.547763	-0.440197	-1.866243
N	1.397172	-0.482049	-2.229525
C	-2.354134	-1.316785	-1.353636
C	-3.517720	-1.355064	-2.156265
H	-4.171696	-0.486085	-2.203170
C	-3.841048	-2.490991	-2.922854
H	-4.735015	-2.494704	-3.543008
C	-3.001058	-3.620434	-2.891235
H	-3.243746	-4.499888	-3.483610
C	-1.836707	-3.605023	-2.100384
H	-1.190538	-4.480202	-2.099174
C	-1.501854	-2.462775	-1.341615
C	-2.504310	-0.202832	1.493737
C	-3.871353	-0.442741	1.776173
H	-4.595784	-0.463406	0.963340
C	-4.317517	-0.675812	3.089895
H	-5.371588	-0.863636	3.283297
C	-3.396148	-0.672291	4.157288
H	-3.736565	-0.854758	5.174159

C	-2.033291	-0.437566	3.901970
H	-1.331213	-0.442457	4.733921
C	-1.585410	-0.209815	2.580889
C	-2.297463	1.843696	-0.795362
C	-3.636353	2.259317	-1.004108
H	-4.449599	1.544436	-0.889387
C	-3.949604	3.587838	-1.340884
H	-4.985176	3.882665	-1.496323
C	-2.918288	4.539684	-1.468348
H	-3.153252	5.570466	-1.724124
C	-1.582743	4.152583	-1.263184
H	-0.797666	4.899276	-1.365398
C	-1.263698	2.815604	-0.929706
C	-0.439587	-3.479724	1.131424
H	-1.168027	-2.987008	1.783584
C	1.246292	-3.471580	-1.150270
H	0.920984	-4.519517	-1.160309
C	0.453475	1.747093	3.030677
H	1.484138	2.090956	2.883868
C	1.171365	-0.980734	3.251866
H	0.958883	-2.029056	3.028002
C	1.194890	2.584520	-2.401566
H	2.275639	2.399196	-2.394134
C	1.303208	3.641764	0.215080
H	1.279971	4.577335	-0.357930
N	2.875585	-0.266592	-0.580192
C	4.242467	-0.180515	-0.303353
C	5.273745	-0.403048	-1.257869
C	4.617573	0.141597	1.027738
C	6.622514	-0.303560	-0.882167
H	5.006085	-0.652912	-2.280774
C	5.969857	0.235989	1.392769
H	3.833128	0.322711	1.758824
C	6.987402	0.014462	0.442886
H	7.395275	-0.478186	-1.628854
H	6.230108	0.485411	2.419863
H	8.034438	0.087382	0.725727
H	2.237773	-0.803437	3.068525
H	0.963095	-0.797537	4.313833
H	0.265420	1.635535	4.106222
H	-0.234549	2.503663	2.639151
H	0.816519	3.812861	1.178978
H	2.351612	3.372791	0.394539
H	1.009326	3.624668	-2.698547
H	0.740493	1.909939	-3.132450
H	1.392478	-3.123755	-2.176883
H	2.207873	-3.406210	-0.627320
H	0.452388	-3.733469	1.718147
H	-0.882592	-4.410517	0.755474

Table 14. DFT optimized coordinates of (α,γ)-N κ^3-bound azide adduct B', [SiP$^{Me}_3$]Ru(N$_3$Ph).

Ru	-0.044099	0.197800	-1.167637
Si	0.857582	-0.068579	0.944017
P	-0.396235	-2.157513	-0.890425
P	2.161136	0.066541	-1.828696

P	-0.138235	2.501726	-0.579497
N	-2.349526	0.384249	-2.567945
N	-1.354340	0.443408	-3.253133
C	-0.071897	-1.478551	1.822787
C	-0.247954	-1.666913	3.213316
H	0.141777	-0.930822	3.914179
C	-0.942943	-2.783077	3.717525
H	-1.078385	-2.902484	4.790445
C	-1.468470	-3.741368	2.830062
H	-2.010187	-4.603297	3.212987
C	-1.305329	-3.573880	1.442187
H	-1.733303	-4.313952	0.769433
C	-0.622597	-2.448980	0.932494
C	2.671641	-0.688168	0.790104
C	3.459686	-1.203624	1.848240
H	3.046167	-1.260436	2.854046
C	4.768693	-1.668516	1.625478
H	5.354481	-2.065730	2.451788
C	5.319854	-1.627878	0.328103
H	6.329912	-1.991089	0.151781
C	4.556615	-1.120370	-0.738524
H	4.990108	-1.096728	-1.736949
C	3.240679	-0.657318	-0.513986
C	0.884313	1.584947	1.892090
C	1.331381	1.762060	3.225451
H	1.670556	0.903403	3.802618
C	1.365937	3.032684	3.826081
H	1.711100	3.143079	4.851792
C	0.958276	4.164584	3.092660
H	0.984140	5.151381	3.549429
C	0.518553	4.014795	1.766060
H	0.208910	4.899019	1.212475
C	0.476978	2.737762	1.159821
C	0.841765	-3.480513	-1.311995
H	1.835243	-3.217175	-0.933933
C	-1.911304	-2.890621	-1.663177
H	-1.954808	-3.977850	-1.520993
C	3.143858	1.574241	-2.290734
H	2.629195	2.133105	-3.081050
C	2.462717	-0.945910	-3.352363
H	2.146795	-1.980603	-3.200307
C	-1.842213	3.223609	-0.487187
H	-2.301694	3.203465	-1.482667
C	0.696925	3.877094	-1.515456
H	0.376364	4.859996	-1.147735
N	-2.238853	0.254397	-1.225381
C	-3.444223	0.166376	-0.522606
C	-4.721489	0.162149	-1.150599
C	-3.389852	0.081881	0.893367
C	-5.891425	0.081542	-0.379087
H	-4.782224	0.226641	-2.232811
C	-4.568248	-0.001003	1.652468
H	-2.421633	0.073061	1.384306
C	-5.831168	-0.000824	1.027727
H	-6.857617	0.082505	-0.880919
H	-4.495701	-0.067782	2.736158

H	-6.741863	-0.064301	1.617952
H	1.863105	-0.521977	-4.167529
H	3.518943	-0.937845	-3.650796
H	4.140668	1.288492	-2.650283
H	3.268201	2.221339	-1.416320
H	1.784648	3.814629	-1.432072
H	0.420897	3.797239	-2.574405
H	-1.806188	4.261175	-0.130915
H	-2.469852	2.635600	0.187084
H	-2.810474	-2.435082	-1.239596
H	-1.894456	-2.677237	-2.738641
H	0.895597	-3.608712	-2.400580
H	0.542291	-4.437093	-0.865534

Table 15. DFT optimized coordinates of α-N η^1-bound azide adduct C, [SiP$^{Me}_3$]Ru(N$_3$Ph).

Ru	-0.568348	-0.106831	0.327476
Si	1.571442	0.090519	-0.538330
P	-0.414814	2.255579	0.198990
P	0.561704	-0.534363	2.333446
P	-0.523239	-2.177207	-0.807554
N	-3.082898	-0.655876	2.033398
N	-3.200876	-1.030299	3.107548
C	1.717054	1.709594	-1.541779
C	2.631351	2.009258	-2.578814
H	3.340626	1.253000	-2.910520
C	2.630670	3.265511	-3.216212
H	3.333106	3.469416	-4.021996
C	1.716786	4.256748	-2.810478
H	1.712477	5.229875	-3.297182
C	0.800876	3.982494	-1.776349
H	0.097813	4.757606	-1.477903
C	0.783678	2.716250	-1.151795
C	2.838056	0.249261	0.897647
C	4.194580	0.634907	0.759764
H	4.587221	0.885622	-0.224738
C	5.049479	0.723715	1.873200
H	6.086298	1.027942	1.743963
C	4.557909	0.422601	3.159656
H	5.213341	0.489076	4.025602
C	3.213696	0.042235	3.321083
H	2.847195	-0.181768	4.321280
C	2.350788	-0.039022	2.203774
C	2.086315	-1.449807	-1.548119
C	3.339584	-1.658317	-2.176555
H	4.106502	-0.887114	-2.126064
C	3.632303	-2.855991	-2.852954
H	4.602099	-2.992913	-3.327011
C	2.669129	-3.883356	-2.907528
H	2.890015	-4.814091	-3.425777
C	1.421308	-3.702343	-2.285332
H	0.688763	-4.505953	-2.332520
C	1.123807	-2.497174	-1.608493
C	0.233520	3.302050	1.601087
H	1.192198	2.900389	1.948213
C	-1.930022	3.254180	-0.222722

H	-1.735979	4.334896	-0.216004
C	0.741304	-2.273821	2.986369
H	-0.250053	-2.702445	3.183809
C	0.019353	0.298343	3.913231
H	0.058967	1.385767	3.793163
C	-1.657093	-2.317180	-2.283562
H	-2.702407	-2.242193	-1.959403
C	-0.921471	-3.811371	0.000782
H	-0.907511	-4.650393	-0.707465
N	-2.881503	-0.252331	0.872187
C	-4.062520	-0.004892	0.086579
C	-5.372305	-0.137073	0.598623
C	-3.857825	0.385403	-1.250610
C	-6.471381	0.124197	-0.238589
H	-5.540625	-0.436373	1.630488
C	-4.962757	0.643333	-2.076751
H	-2.837394	0.477182	-1.614857
C	-6.274554	0.514711	-1.577594
H	-7.479135	0.022398	0.156988
H	-4.798935	0.942824	-3.108989
H	-7.128029	0.714971	-2.219844
H	-1.016600	0.011798	4.135837
H	0.640602	0.016159	4.773780
H	1.329151	-2.302292	3.913935
H	1.248514	-2.891518	2.236490
H	-0.208717	-4.018531	0.805458
H	-1.925954	-3.747891	0.440052
H	-1.516863	-3.268890	-2.814011
H	-1.449675	-1.494818	-2.977801
H	-2.308681	2.968488	-1.209961
H	-2.712145	3.039008	0.516102
H	-0.479431	3.282895	2.436083
H	0.382848	4.343929	1.287969

Table 16. DFT optimized coordinates of (α,β)-N η^2-bound azide adduct D, [SiP$^{Me}_3$]Ru(N$_3$Ph).

Ru	-0.123920	0.214546	-1.105705
Si	0.985127	-0.078967	0.894977
P	-0.413314	-2.153705	-0.847405
P	2.012505	0.124741	-1.978168
P	-0.185922	2.510188	-0.459698
N	-2.212489	0.428553	-2.372790
N	-3.027152	0.540234	-3.256822
C	0.143629	-1.505870	1.833696
C	0.088728	-1.708726	3.232312
H	0.529958	-0.974907	3.904336
C	-0.549574	-2.836908	3.782809
H	-0.591157	-2.967804	4.862105
C	-1.139401	-3.792782	2.933901
H	-1.636421	-4.664740	3.353046
C	-1.098660	-3.610172	1.538814
H	-1.575492	-4.348733	0.898044
C	-0.473860	-2.472826	0.984035
C	2.778523	-0.683273	0.562880
C	3.666753	-1.214443	1.529798
H	3.350561	-1.297559	2.568565

C	4.952383	-1.661232	1.173634
H	5.616923	-2.071246	1.931245
C	5.377790	-1.585150	-0.168653
H	6.369632	-1.933523	-0.448168
C	4.512933	-1.061685	-1.146401
H	4.851022	-1.011078	-2.179998
C	3.220165	-0.617696	-0.788301
C	1.092251	1.554046	1.871665
C	1.671018	1.706827	3.156522
H	2.076132	0.839778	3.675742
C	1.753962	2.964143	3.779990
H	2.201440	3.056113	4.767260
C	1.261759	4.106936	3.118806
H	1.324122	5.083544	3.593582
C	0.690427	3.981315	1.840764
H	0.316725	4.873758	1.342778
C	0.600871	2.717610	1.212120
C	0.794219	-3.455833	-1.400520
H	1.814385	-3.188383	-1.105662
C	-1.988194	-2.885681	-1.490548
H	-2.024078	-3.971746	-1.338216
C	2.935747	1.656456	-2.485458
H	2.349036	2.228959	-3.213526
C	2.202983	-0.848070	-3.547901
H	1.873917	-1.880577	-3.407320
C	-1.885367	3.190737	-0.172532
H	-2.446212	3.192009	-1.114900
C	0.524274	3.924177	-1.440628
H	0.249464	4.891867	-1.002287
N	-2.280315	0.265747	-1.047329
C	-3.496018	0.149902	-0.365928
C	-4.778101	0.216967	-0.978127
C	-3.424418	-0.043660	1.043129
C	-5.939809	0.096316	-0.192498
H	-4.860223	0.363517	-2.049224
C	-4.591052	-0.161882	1.809377
H	-2.447053	-0.106130	1.513355
C	-5.862731	-0.092250	1.199992
H	-6.911879	0.151825	-0.679152
H	-4.508511	-0.311366	2.884004
H	-6.767063	-0.183685	1.796473
H	-2.849153	-2.424994	-0.998505
H	-2.060966	-2.680566	-2.565368
H	0.543995	-4.423874	-0.948448
H	0.754564	-3.563682	-2.492024
H	3.240057	-0.853138	-3.907668
H	1.570114	-0.389057	-4.318214
H	3.901279	1.393867	-2.936323
H	3.127272	2.283001	-1.607993
H	1.614149	3.865518	-1.494397
H	0.120238	3.881090	-2.460089
H	-1.834068	4.216739	0.213767
H	-2.428752	2.566854	0.541701

Table 17. DFT optimized coordinates of (β,γ)-N η^2-bound azide adduct E, [SiP$^{Me}_3$]Ru(N$_3$Ph).

Ru	0.518861	-0.201697	-0.216163
Si	-1.873699	0.133067	-0.000800
P	0.343789	-0.114708	2.154678
P	0.301655	1.973471	-1.135119
P	-0.338810	-2.233353	-1.108294
N	2.601507	-0.070337	-0.100918
N	3.571988	0.786035	-0.054541
C	-2.418114	-0.088333	1.822849
C	-3.761257	-0.163364	2.269780
H	-4.576821	-0.135643	1.549475
C	-4.071572	-0.296683	3.634735
H	-5.109753	-0.356337	3.954574
C	-3.036041	-0.358079	4.589645
H	-3.271803	-0.460283	5.646567
C	-1.696393	-0.296471	4.168752
H	-0.903609	-0.355134	4.912236
C	-1.385181	-0.169169	2.795763
C	-2.410287	1.885421	-0.548825
C	-3.715580	2.429255	-0.448383
H	-4.515576	1.849761	0.008172
C	-4.003695	3.726016	-0.908979
H	-5.012256	4.124061	-0.819982
C	-2.984153	4.514181	-1.481543
H	-3.204417	5.517152	-1.840006
C	-1.678710	4.002502	-1.575402
H	-0.893559	4.623807	-2.002365
C	-1.391259	2.699683	-1.109202
C	-2.875443	-1.140314	-1.023565
C	-4.258780	-1.084741	-1.324625
H	-4.851407	-0.227493	-1.012399
C	-4.890022	-2.113266	-2.047463
H	-5.952126	-2.046664	-2.273576
C	-4.147245	-3.229368	-2.483819
H	-4.634081	-4.026145	-3.041571
C	-2.771390	-3.302374	-2.204523
H	-2.202128	-4.161498	-2.554883
C	-2.138380	-2.262463	-1.488015
C	1.073936	1.355954	3.019814
H	0.527988	2.260981	2.729813
C	1.197118	-1.495108	3.051950
H	1.163294	-1.369105	4.141971
C	0.807558	2.073344	-2.917432
H	1.855541	1.761662	-3.007492
C	1.358643	3.297370	-0.392601
H	0.992907	3.541121	0.611301
C	-0.064847	-3.765543	-0.106334
H	1.000463	-3.834373	0.142894
C	0.480668	-2.692509	-2.704089
H	0.160357	-3.678667	-3.066180
N	2.396031	-1.284435	-0.174838
C	4.888054	0.264370	-0.092604
C	5.911150	1.250071	-0.022151
C	5.268889	-1.100839	-0.187924
C	7.264273	0.888269	-0.045500

H	5.612603	2.293048	0.051330
C	6.632741	-1.452658	-0.209899
H	4.510099	-1.872469	-0.245013
C	7.637514	-0.470599	-0.139511
H	8.029159	1.660388	0.009515
H	6.907123	-2.503477	-0.283202
H	8.687397	-0.753385	-0.157556
H	1.564982	-2.704244	-2.542246
H	0.250027	-1.941316	-3.467696
H	-0.369128	-4.670047	-0.649405
H	-0.641413	-3.702432	0.823646
H	0.729209	-2.449978	2.788465
H	2.244469	-1.530885	2.729359
H	2.119775	1.467898	2.708061
H	1.032360	1.255491	4.112697
H	1.359335	4.211451	-1.000931
H	2.379315	2.905614	-0.305861
H	0.706887	3.093386	-3.312323
H	0.187353	1.398149	-3.517296

Table 18. DFT optimized coordinates [SiP$^{Me}_3$]Ru(N_2).

Ru	0.163647	-1.318768	-0.525225
Si	-0.068165	0.968758	0.037444
P	-2.113003	-1.016489	-1.099797
P	0.146006	-1.592962	1.800221
P	2.351451	-0.625634	-1.080076
N	0.362740	-3.287578	-1.009190
N	0.480350	-4.380159	-1.247254
C	-1.553936	1.731295	-0.893607
C	-1.813077	3.104702	-1.121032
H	-1.093704	3.853209	-0.794111
C	-2.979111	3.531917	-1.783438
H	-3.151012	4.592292	-1.956793
C	-3.923768	2.583998	-2.223255
H	-4.828688	2.908014	-2.732721
C	-3.687335	1.213641	-2.009975
H	-4.421764	0.491973	-2.363054
C	-2.507197	0.781550	-1.364345
C	-0.485407	1.131879	1.905776
C	-0.892098	2.325032	2.553851
H	-0.998361	3.243668	1.978851
C	-1.184049	2.351129	3.929239
H	-1.499172	3.278388	4.403475
C	-1.073134	1.171278	4.692908
H	-1.298314	1.184675	5.757176
C	-0.675848	-0.025587	4.071531
H	-0.598929	-0.930573	4.671646
C	-0.388097	-0.053981	2.687207
C	1.550998	1.941764	-0.268097
C	1.759395	3.322067	-0.021088
H	0.948149	3.931456	0.373280
C	3.004584	3.931797	-0.255549
H	3.138718	4.993227	-0.057659
C	4.081615	3.163481	-0.741113
H	5.047897	3.628620	-0.923570

C	3.903087	1.790557	-0.984603
H	4.744726	1.207784	-1.354388
C	2.650719	1.176843	-0.751681
C	-3.531040	-1.554972	-0.020153
H	-3.448005	-1.070516	0.959817
C	-2.613350	-1.802220	-2.708502
H	-3.661887	-1.606953	-2.969598
C	1.728481	-1.999604	2.693920
H	2.146528	-2.932064	2.293529
C	-0.950016	-2.913359	2.517751
H	-1.992412	-2.721964	2.242913
C	2.714526	-0.754778	-2.901560
H	2.665149	-1.807727	-3.207586
C	3.881451	-1.440047	-0.401746
H	4.803366	-1.046578	-0.849578
H	-1.970839	-1.425300	-3.512361
H	-2.467234	-2.887300	-2.633115
H	-0.878470	-2.976628	3.611741
H	-0.656071	-3.882295	2.093778
H	2.453673	-1.194078	2.532537
H	1.571596	-2.115072	3.774954
H	3.931155	-1.300865	0.683450
H	3.825934	-2.516655	-0.608094
H	3.706801	-0.355990	-3.153300
H	1.955935	-0.197151	-3.461990
H	-4.501947	-1.289344	-0.458886
H	-3.491800	-2.642915	0.120610

Table 19. DFT optimized coordinates [SiP$^{Me}_3$]Ru(NPh).

Ru	-0.442387	0.181575	-1.022685
Si	1.030960	-0.054300	0.778849
P	-0.447314	2.464161	-0.356870
P	1.592196	0.111791	-2.208488
P	-0.630747	-2.171841	-0.616391
N	-2.341514	0.242596	-1.104130
C	-6.261423	0.039911	0.411647
C	2.762523	-0.654136	0.189625
C	-3.580509	0.179211	-0.602874
C	0.369924	-1.444598	1.901734
C	1.295610	1.603948	1.682150
C	0.657621	2.740792	1.110199
C	-0.386814	-2.435479	1.207690
C	2.117821	1.799398	2.820074
H	2.638942	0.953042	3.264603
C	1.658378	4.191261	2.811192
H	1.795457	5.181147	3.240835
C	2.297510	3.074159	3.385291
H	2.933085	3.199722	4.259293
C	-0.015908	3.875779	-1.491832
H	-0.199953	4.848873	-1.018360
C	-0.705587	-3.682187	3.288782
H	-1.122988	-4.535515	3.818835
C	0.518087	-3.455584	-1.321412
H	0.317238	-3.585242	-2.392683
C	2.386001	1.658935	-2.871111

H	1.685262	2.187810	-3.528444
C	0.561894	-1.599758	3.294133
H	1.116300	-0.847258	3.852038
C	0.843939	4.022631	1.677959
H	0.359380	4.895280	1.244416
C	4.229120	-1.007482	-1.758559
H	4.408308	-0.954942	-2.831194
C	-6.029566	0.257008	-0.968654
H	-6.874741	0.371126	-1.645282
C	-4.726687	0.323452	-1.471540
H	-4.538729	0.485505	-2.530825
C	-0.906875	-3.549227	1.901418
H	-1.484897	-4.308088	1.378431
C	2.994963	-0.586992	-1.213249
C	1.586472	-0.893714	-3.771284
H	2.561756	-0.887889	-4.275730
C	0.025657	-2.702638	3.987291
H	0.172365	-2.795788	5.061417
C	3.794805	-1.166318	1.013752
H	3.637964	-1.252426	2.088055
C	-2.255754	-2.979508	-0.978808
H	-2.228653	-4.058649	-0.781228
C	5.021077	-1.591216	0.470353
H	5.798447	-1.987378	1.120554
C	5.240545	-1.510282	-0.920383
H	6.186575	-1.840179	-1.344370
C	-2.071149	3.092002	0.274048
H	-2.809370	3.074382	-0.535653
C	-5.157553	-0.109397	1.285853
H	-5.328970	-0.279206	2.347400
C	-3.847604	-0.040304	0.801357
H	-2.995670	-0.156819	1.468005
H	-7.277226	-0.012548	0.796208
H	-1.976506	4.116490	0.655989
H	-2.438765	2.444363	1.074918
H	-3.049998	-2.522371	-0.382499
H	-2.495551	-2.819743	-2.036534
H	-0.643873	3.802935	-2.388863
H	1.032565	3.829226	-1.797545
H	0.837673	-0.469180	-4.451913
H	1.305861	-1.928770	-3.558138
H	3.294357	1.419881	-3.439231
H	2.664226	2.318183	-2.041669
H	1.561985	-3.152202	-1.190148
H	0.369179	-4.420699	-0.820387

Table 20. DFT optimized coordinates of singlet nitrene ^{1}PhN.

N	2.404623	-0.000002	0.000093
C	1.093414	0.000001	-0.000087
C	0.339572	1.249315	0.000056
H	0.894327	2.183364	0.000136
C	-1.052187	1.229252	0.000023
H	-1.602553	2.167202	0.000059
C	-1.762602	0.000000	-0.000048
C	-1.052189	-1.229252	-0.000047

H	-1.602550	-2.167205	-0.000065
C	0.339572	-1.249313	-0.000017
H	0.894326	-2.183362	0.000009
H	-2.849399	0.000001	-0.000063

Table 21. DFT optimized coordinates of triplet nitrene ^{3}PhN.

N	-2.415595	-0.000101	0.000184
C	-1.083375	0.000048	-0.000234
C	-0.341334	-1.242124	0.000052
H	-0.895007	-2.177136	0.000200
C	1.055009	-1.226258	0.000037
H	1.602833	-2.165616	0.000144
C	1.763334	-0.000015	-0.000081
C	1.054885	1.226232	-0.000038
H	1.603189	2.165325	0.000013
C	-0.341371	1.242249	-0.000015
H	-0.894974	2.177292	0.000080
H	2.850235	0.000047	-0.000054

Table 22. DFT optimized coordinates of N_2.

N	0.000000	0.000000	0.552652
N	0.000000	0.000000	-0.552652

Table 22. DFT optimized coordinates of the transition state for the reaction: [SiP$^{Me}_3$]Ru(N_3Ph) (structure A) → [SiP$^{Me}_3$]Ru(N_2) + ^{3}PhN.

Ru	0.291642	0.044728	0.187411
Si	-1.988837	0.038161	-0.404935
P	0.007237	-2.267506	-0.303184
P	-0.611978	0.104879	2.284695
P	0.148163	2.310210	-0.465161
N	2.225445	-0.014702	-0.268040
N	3.304848	-0.044540	-0.694601
N	4.535796	-0.017484	0.757775
C	-2.281252	-1.360840	-1.664890
C	-3.306531	-1.449874	-2.635625
H	-4.013368	-0.630473	-2.753341
C	-3.422290	-2.573578	-3.476123
H	-4.209945	-2.615922	-4.225539
C	-2.514629	-3.642596	-3.347536
H	-2.600394	-4.514268	-3.992546
C	-1.486500	-3.575717	-2.388402
H	-0.786681	-4.405140	-2.309519
C	-1.354653	-2.440551	-1.558859
C	-3.073303	-0.412174	1.116981
C	-4.443098	-0.772100	1.107208
H	-4.986426	-0.812404	0.164254
C	-5.119374	-1.102813	2.295894
H	-6.170314	-1.383079	2.266126
C	-4.432904	-1.078725	3.527700
H	-4.952471	-1.337209	4.447810
C	-3.071947	-0.725409	3.562235
H	-2.551147	-0.715123	4.518192
C	-2.392801	-0.399552	2.366566

C	-2.553051	1.756844	-1.014275
C	-3.861418	2.097783	-1.439244
H	-4.639966	1.336945	-1.461142
C	-4.191615	3.411230	-1.817695
H	-5.203271	3.648910	-2.139549
C	-3.210883	4.422042	-1.770335
H	-3.460617	5.440935	-2.057786
C	-1.907048	4.109705	-1.347164
H	-1.160765	4.900932	-1.313690
C	-1.572045	2.788687	-0.970363
C	-0.458293	-3.564342	0.943938
H	-1.349975	-3.250091	1.498131
C	1.459066	-3.081180	-1.113332
H	1.262951	-4.131212	-1.363542
C	-0.646188	1.718093	3.202929
H	0.370919	2.119978	3.281831
C	0.244163	-0.956941	3.541112
H	0.181342	-2.010874	3.255584
C	1.101973	2.601437	-2.029730
H	2.168927	2.430218	-1.844093
C	0.742560	3.751707	0.545681
H	0.736514	4.688845	-0.025684
C	5.795464	-0.031185	0.286080
C	6.177837	-0.092311	-1.109388
H	5.395229	-0.131454	-1.857412
C	7.524684	-0.101779	-1.481856
H	7.789366	-0.148870	-2.536599
C	8.550513	-0.051066	-0.507355
C	8.208948	0.009108	0.865568
H	8.995142	0.047675	1.617023
C	6.869182	0.018470	1.260522
H	6.591658	0.063695	2.310746
H	1.725278	-2.537499	-2.026177
H	2.316923	-3.034669	-0.432320
H	-0.183460	-0.835406	4.545441
H	1.302576	-0.671622	3.569142
H	-1.274472	2.437032	2.665703
H	-1.057575	1.585819	4.212302
H	0.123901	3.881415	1.439018
H	1.772070	3.545471	0.863852
H	0.957729	3.623187	-2.404350
H	0.770081	1.891674	-2.795333
H	-0.672205	-4.522669	0.453591
H	0.367897	-3.709127	1.651632
H	9.594679	-0.058804	-0.811403

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